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Modeling trihalomethane formation in bromide-containing surface water undergoing conventional treatment

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MODELING TRIHALOMETHANE FORMATION IN BROMIDE-CONTAINING SURFACE WATER UNDERGOING CONVENTIONAL TREATMENT

A Thesis

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By

Maureen McBride Smith

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ABSTRACT

Trihalomethanes (THMs) have been established as significant by-products from the chlorination of raw surface water. The reaction has been demonstrated to be influenced by a number of source water quality and treatment parameters. This study uses empirical data to examine the formation of total THMs (TTHMs) during conventional treatment of California Aqueduct water. The water quality (pH, NTU, temperature, MPN and bromide concentration) and treatment (total chlorine dose and application point, flow rate, and dosages of treatment chemicals) variables were examined for their relative contributions to TTHM formation. Linear regression analysis was used for model development employing significant variables to predict TTHMs. Raw water bromide was found to have a significant influence on TTHMs when considering mass but not molar concentrations. It was determined that bromide alone is not a good surrogate for TTHMs. The most influential variable on TTHMs is chlorine dose. Raw water chlorination is also highly correlated with increasing TTHMs. Both chlorination parameters increased mass and molar concentrations of TTHMs, with a slightly higher correlation with molar than mass concentration. Models to predict TTHMs were developed which included bromide, raw water chlorination and total chlorine dose. The models were found to predict within $\pm$ 20% of measured TTHMs for up to 70% of the database and 61% of new data.

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INTRODUCTION

Public concern over chemical contamination of the environment generally and particularly of our water supply is great. The possibilities of waterborne diseases and chemical carcinogens in our drinking water are areas of active and sometimes emotionally charged interest (1,2,3,4). Concerns over the toxicology of disinfectants and disinfectant by-products (DBPs) in our drinking water have prompted much research (1,3,5,6) and government regulation (7,8,9), although not always in that order. Public interest and fear have motivated the United States government to enact laws mandating standards of quality for drinking water overseen by the United States Environmental Protection Agency (EPA).

The first federal standards for drinking water were issued in 1914 for interstate water supply protection. In 1962 mandatory limits were adopted regarding hazardous chemicals and biological contaminants in interstate water supplies (4). The Safe Drinking Water Act (SDWA) of 1974 applied primary drinking water standards to all public water supplies in the United States (7,10). The SDWA also mandated that the EPA conduct a comprehensive survey of public water supplies to determine the nature, extent, source, and means of control of contamination by substances suspected of being carcinogenic (7,11). Prompted by an

earlier report of organic chemicals in New Orleans drinking water, this study involved the water supplies of 80 cities in the National Organics Reconnaissance Survey (NORS) (11).

Reports of organohalides in drinking water appeared as early as 1970 but technical and analytical limitations prevented the identification of their source (12,13). In 1974, J.J. Rook (14) and T.A. Bellar *et al* (12) identified the presence of chlorinated organics and other haloforms in drinking water supplies. They identified the source as being the result of the chlorination process during water treatment and noted that the organohalides were in highest concentration where raw surface waters were used (12,14). Rook proposed the reaction involved the chlorination of humic substances ,or organic matter, in the water (14,15).

The NORS looked for the presence of 1,2-dichloroethane, carbon tetrachloride and the four compounds identified as trihalomethanes (THMs): chloroform (trichloromethane). bromodichloromethane, dibromochloromethane, and bromoform (tribromomethane). All of the systems tested had chloroform in their drinking water and while all did not have the brominated compounds enough did so that the result was to "consider their occurrence widespread" (11). The other two compounds surveyed, 1,2-dichloroethane and carbon tetrachloride, did not occur as frequently. When they were found, one-third of the time they were in the raw water as well. The conclusion of the NORS was that THMs are

ubiquitous in chlorinated drinking waters and result from chlorination. Significantly, as will be discussed below, all of the systems studied were using surface water sources which provide precursors necessary for the formation of THMs.

The results of the NORS inspired the EPA's promulgation of the November 26, 1979 establishment of a maximum contaminant level (MCL) for total THMs (TTHMs) (7,8,13,16). The MCL for the summation of all four compounds, or TTHMs, was set at 0.10 mg/L (milligrams per liter) as a running average.

Public concern over the drinking water supply still was not satisfied by existing regulations. This led to the development of amendments to the Safe Drinking Water Act (SDWA) which were adopted by the United States Congress June 19,1986(17). As recently expressed by G.J. Smith, 1990, the motivation for regulation is public fear:

> *"From a regulatory perspective, we see that the American public is very concerned about drinking water health effects, especially since water has been accused of being the source of every malady from Alzheimer's disease to cancer to heart attacks" (18, p.30).*

The SDWA amendments required the EPA to regulate 83 contaminants by June 1989 and 25 additional contaminants every 3 years thereafter (8,17). The first group of 25 contaminants proposed for regulation by the EPA included THMs, disinfectants and DBPs (8,19). The possible levels

for the establishment of a new TTHM standard are in the 5-50 *ug*/L (micrograms per liter) range. Alternatively, the TTHMs may be regulated in the 50-100 *ug*/L range but include variable individual THM MCLs (20). Either way, the reduction of MCL for TTHMs or individual THM MCLs will force major changes in disinfection and water treatment practices accompanied by greatly increased costs (8,19,21).

The cost of compliance with the 0.10mg/l TTHM rule involved capital expenditures of $31 to $102 million and yearly operating costs of $8 to $29 million for utilities serving more than 10,000 people (22). The costs for compliance with the new rule are estimated to exceed those figures drastically and will depend upon the actual MCL established (8,19,22,23). It is also likely that there will be a large number of utilities that will not be capable of meeting a significantly lower MCL requirement with poor quality source waters and available technology (8,19,22,24,25,26,27,28,29).

As stated in the theme introduction of the October 1990 issue of the Journal of the American Water Works Association (AWWA), the water industries' foremost publication:

> *"'Ingest a tiny bit of this every day for 70 years and your odds of getting cancer are 1 in a million, if our mouse test data and dose-response extrapolation models can be trusted,' is hardly a hair-raising risk assessment, especially when such verdicts have been handed down on just about everything in the food chain. People could be more likely to die of a heart attack when they hear the price tag for regulating such poisons" (20,p.43).*

The above quote identifies the significant controversy surrounding the existing and proposed MCLs for TTHMs versus the need or justification for regulations. Water chlorination for disinfection has been used since the turn of the century and its significance in reducing waterborne diseases has been well documented (30,31), the toxicology of THMs is still under investigation.

In 1978 representatives of the EPA wrote that if a chemical was "suspect" it was reason enough for regulation (9). As the number of chemicals and DBPs found in water increases, the rapidly developing science of risk assessment is of utmost importance (8,20,32,33,34). Science is needed to evaluate whether there are significant risks involved with the presence of these chemicals in drinking water or not (4,8,13,19,22,35). Justification for the great expenditures expected must come from the need for the protection of public health, not from unfounded public panic.

Concurrently, research regarding the techniques of minimization or removal of chemicals and contaminants in our drinking water is also needed. Since the 1974 identification of DBPs, particularly the THMs, research and interest in the water industry has grown tremendously. In the Journal of the American Water Works Association, theme issues where the entire journal was devoted to THMs or DBPs

have been presented in 1978, 1982, 1984 and 1990 (23,36,37,38). In 1984, just 10 years after the identification of THMs in drinking water, the AWWA publications catalog listed 152 titles under the heading trihalomethanes (37). The research on THMs involves several necessary areas, ranging from first the identification and characterization of the reactions and the precursors, to the variables that influence the rate and products of the reactions, and finally to treatment practices that can be used to limit or eliminate the reactions.

THE REACTION

Rook (14,39) proposed a simplified mechanism for THM formation involving the reaction of chlorine with precursor material. He identified naturally occurring humic substances as the probable organic precursors but did not exclude the possibility of others. Rook also noted that the presence of bromide in natural waters contributed to the reaction that formed the brominated THMs.

Drinking water is most usually chlorinated using gaseous chlorine (Cl_2). When elemental chlorine is dissolved in water it hydrolyses rapidly and extensively as shown in equation 1 (40,41):

equation 1: $Cl_2 + H_2O$ ---> HOCl + H+ + Cl-

The resulting hypochlorous acid is a very good oxidant and also substitutes Cl into organic molecules to form organohalides (40,41,42,43,44). Hypochlorous acid and chlorite ion exist in equilibrium in water dependent upon the pH, equation 2:

equation 2: HOCl <==> H+ + OCl-

The bromide ion and chlorine react as in equation 3(45):

equation 3: Cl_2 + 2Br- ---> Br_2 + 2Cl-

Bromine dissolves in water as seen in equation 4 (46):

equation 4: $Br_2 + H_2O$ <==> H+ + Br- + HOBr

OR $2Br_2 + 2H_2O$ <==> 4H+ + 4Br- + O_2

Equation 5 exhibits the reaction that occurs between hypochlorous acid and bromide:

equation 5: $HOCl + Br^- \rightarrow HOBr + Cl^-$

The substitution reactions to form organohalides occur with hypochlorous or hypobromous acid and organic precursor material as seen in equations 6 and 7 (40,41,42,43,44).

equation 6: $HOCl + \text{precursor} \rightarrow CHCl_3$

equation 7: $HOBr + Cl^- + \text{precursor} \rightarrow CHCl_2Br + CHClBr_2 + CHBr_3$

In comparing the kinetics of these reactions it has been determined that hypochlorous acid acts preferentially as an oxidant when compared to hypobromous acid which performs substitution reactions preferentially and more rapidly than hypochlorous acid (15,40,41,42,43).

INFLUENCING VARIABLES

The haloform reaction is extremely sensitive to a great number of parameters. To attempt control over the reaction these varying influences must first be clarified.

Paramount is the source water quality which is characterized by the bromide concentration, pH, temperature and type and amount of components accounting for the total organic carbon (TOC). Treatment parameters such as pH during chlorination, point of chlorination, contact time and chlorine dose influence the reaction rate and concentration of THMs formed as well.

BROMIDE: Rook postulated in 1974 (14) that if bromide was present in water chlorine would oxidize it and thus allow the brominated THM compounds to be formed. As demonstrated in equations 3, 4, 5 and 7, this is indeed the case. The influence of the bromide ion on the reaction rates and yield of the reactions has since been demonstrated. In 1978 it was reported that bromide seemed to react with precursors more rapidly (47) and investigation into bromide's effect on the yield of the reactions was called for (15). By 1982 the fact that increasing bromide concentration in raw waters resulted in increased TTHMs had been well documented by numerous studies (e.g. 44,48,49,50). Bromide concentration in the microgram per liter range affects not only the yield of the reaction but also the rate and product distribution among the four forms of THMs

(51,52,53). Bromination of organics is significantly favored over their chlorination (42,46,54), and when bromide is present, it preferentially shifts the reaction to bromine containing THMs (28,42,43,51,55,56). Moreover it has been shown that the bromide ion shifts the overall organohalide DBP reactions to THM products containing bromine (24,56,57).

It has been demonstrated that 40-60% of the bromide in raw water is incorporated into THMs during chlorination whereas only 10-20% of the raw water chloride is (28,43).

The effect of bromide on the THM reaction has been studied extensively, and the fact that the concentration of THMs increases with increasing bromide concentration has been well established (24,28,42,43,51,52,53,55,56,57). However, it should be noted that these studies, and the conclusions drawn from them, dealt with weight concentrations. The atomic weight of chlorine is 35.453 while that of bromine is more than twice that at 79.904. Therefore, the more highly brominated THMs weigh more than the chlorinated ones which may account for the observed increase in weight concentration of TTHMs. It would be interesting to review the past research efforts in this light, determining molar amounts of product to see if bromide concentration really increases the molar concentration of TTHMs or simply increases the total weight of the compounds. This study will evaluate results in both weight concentration and molar concentration terms.

pH: According to the 1975 NORS, higher pH levels at the point of chlorination will result in higher TTHMs production (11). Numerous studies followed confirming this relationship, and the direct influence of pH upon reaction yield was clearly demonstrated (15,39,44,47,48,53,54,58,59, 60,61,62). Both in the experimental laboratory and treatment plant operations it has been conclusively demonstrated that if the pH at chlorination is raised more TTHMs are produced, whereas if it is lowered less TTHMs are formed.

The reports do not try to explain the mechanism of the pH influence but the empirically derived evidence has been vast. Aqueous chlorine is a better oxidizer at lower pH shifting the equation to the right to form more hydrochlorous acid (see equation 1) under more acidic conditions (31). This effect is evident in the oxidation of bromine by chlorine which slows at higher pH values (43). One could postulate that since hypochlorous acid is a more active oxidizer at lower pH more of the organic precursor material is oxidized before substitution reactions take place, thereby minimizing the yield by reducing the precursor concentration. Knowledge of the mechanism of action is not immediately necessary to gain beneficial use of the direct relationship between pH and TTHM production in raw water treatment.

The increase in TTHMs as a function of pH has been demonstrated both in the presence (15,39,44,54) and absence (15,39,58,59,61) of bromide.

TEMPERATURE: Temperature has a direct influence on TTHM yield. Laboratory experiments and plant scale studies have shown that as water temperature increases the reaction rate and product concentrations increase and the reverse holds true as well (15,24,28,39,44,48,49,53,63,64,65).

ORGANIC PRECURSORS: The NORS determined that the dominant factor influencing the creation of chlorination by-products was the general organic level of the water, measurable as TOC (11). The fact that higher average TTHMs are observed where surface water is chlorinated was also noted by Rook, Bellar *et al*, the NORS and others (11,12,14,39,58). Raw water, water before any treatment has been applied, and most notably raw surface water, contain high levels of TOC (24,39,44,54,66).

The precursors for the THM reaction are the compounds containing organic carbon which exist in natural waters. Humic substances, humic and fulvic acids, are the most abundant precursors (28,42,67,68,69,70). Algae biomass (71,72,73) and, particularly, algal extracellular products (72,73,74), proteins (74), as well as man made synthetic organic chemicals (75) and some coagulant aids added during water treatment (51,76) can also serve as precursors.

Humic substances are chemically complex polyelectrolytes or macromolecules which are amorphous, acidic, hydrophilic, and predominately aromatic (28,67,68,77). In natural waters humic substances are negatively charged and are usually colloidal (68,77,78,79,80,81). The charge density and configuration of the humic macromolecules are more stable at higher pH levels (77,82). The molecular weight of humic substances range from a few hundred to tens of thousands and their specific compositional characteristics will vary greatly reflecting the different soil, vegetative and environmental conditions from which they originate (24,28,67).

As in any chemical reaction the concentration of the reactants will determine the concentration of products. The NORS results showed the relationship of concentration of organic matter in the water to TTHMs when is was noted that chlorination of raw water yielded higher average TTHMs than chlorination of treated water (11). In 1976, Rook (39) demonstrated a direct relationship between fulvic acid concentration and TTHMs. Using various analytical methods, all essentially measuring the amount of organic carbon in the water, this effect has been confirmed numerous times (44,49,53,54,61,66,70,83,84). THM formation is influenced by the source and type of organic precursors as well as their abundance.

In 1980, Hoehn *et al* (72) and Briley *et al* (73) reported that algae and algal extracellular products (ECP) could be THM precursors. Hoehn *et al* (72) found that dissolved ECP were more reactive than suspended biomass and both studies showed different degrees of reactivity related to different stages in the algal life cycle. A later study in 1988 (74) found algal proteins to be THM precursors and that more proteins are available during algae blooms. In light of the effect of elevated pH and temperature on increased THM yield, it is interesting to note that water pH elevation is observed with the growth and bloom of aquatic algae during warm weather (85,86,87). In this situation, higher pH results from intense photosynthetic activity of the algae, in which the carbonic acid-bicarbonate-carbonate balance is shifted to the right (88).

The source-related properties and THM reactivity evident in the algal studies have also been observed with other humic substances (49,54,66). Collins *et al* (68) concluded that source related properties of aquatic organic material affect their reactivity in forming THMs. These properties include molecular weight, functional group carboxylic acidity and humic substance content.

Molecular weight as a significant property of humic substances' propensity for halogenation was examined by Trussell and Umphres (15). They found that the higher molecular weight humic acids were more reactive with

chlorine than the lower molecular weight fulvic acids. Numerous other researchers have confirmed that one of the most important attributes of humic substances reactivity in the THM reaction is molecular weight (28,67,68,69,89).

CHLORINE: Chlorine is an essential part of the reaction to form THMs. As seen in the reaction equations (see equations 1-7) chlorine is involved as an oxidant as well as being substituted into organic molecules to form THMs. Chlorine has been used in drinking water since the late 1800s as a very effective disinfectant and oxidizer for the control of taste and odor problems (31).

In 1974 it was discovered that chlorinated drinking water contained organohalides, especially THMs (12,14). The 1975 NORS conclusions revealed that maintaining a chlorine residual above 0.4 mg/L increases the average TTHMs (11). Experiments that followed showed there is indeed a relationship between increasing chlorine dose and increasing TTHMs (15,39,42,44,48,49,53,54,61).

The NORS (11) observed that chlorination of raw water resulted in higher TTHMs. The importance of point of chlorination in the treatment train involves not only the amount of precursors available (58,90) but also contact time.

Rook (39) studied the THM reaction in 1976 and determined that the reaction occurred very rapidly at first then a slower but steady increase in products, especially

chloroform, followed. This pattern of rate of formation and increase in concentration with time has been very conclusively confirmed (42,44,49,54,59). Contact time is not as significant in rapidly forming bromoform, it has been shown that bromination does not significantly increase after the first day (56).

REDUCING TRIHALOMETHANES

The development of knowledge of presence of THMs in drinking water led to attempts to reduce their occurrence. Regulations promulgated by the EPA on Nov. 29, 1979, establishing a MCL and monitoring requirements for TTHMs, were accompanied by suggested methods to meet the MCL (7). The best available technologies listed to meet the 0.10 mg/L limit were to (7):

1. Improve clarification to remove precursors.
2. Use chloramine as an alternate disinfectant.
3. Use chlorine dioxide as an alternate disinfectant.
4. Move the point of chlorination.
5. Use powdered activated carbon to remove precursors or to remove the THMs after they are formed.

Additional methods suggested as possibly beneficial were (7):

1. Off-line storage for THM precursor reduction.
2. Use aeration for THM removal where appropriate.
3. Use clarification if not currently used.
4. Find alternative sources of raw water (presumably with lower TOC level).
5. Use ozone as an alternate or supplemental disinfectant.

CLARIFICATION: Optimization of precursor removal with the goal of lowering TTHMs has been the focus of numerous laboratory-scale and plant-scale studies(68,91,92). Clarification has been shown to be variably effective for the removal of THM precursors(47). In a conventional treatment plant design, raw water enters the plant mixing chamber where chemical coagulants are added. The coagulant most commonly used is alum (aluminum sulfate), but also used are ferric or other aluminum salts and/or organic polymers.

The coagulant forms a floc which attracts particles and large molecules in the water and then settles out. After a settling period the clarified water is filtered to remove any residual turbidity. The purpose of coagulation is to destabilize colloids and particles, to oxidize precursors and then to precipitate or adsorb these compounds (78,79). One proposed mechanism of alum coagulation is that the positive aluminum hydroxide coats the negatively charged particles (including the negatively charged humic substances) which then form a precipitate that settles out (78,80,81). Sometimes coagulant aids, such as organic polyelectrolytes, are used to assist in the flocculation process.

The type and source of precursor material has been shown to affect alum's efficiency of removal (79,93,94,95). Alum has been found to remove higher molecular weight compounds more efficiently than those of lower molecular weight (28,70,79). Lower molecular weight compounds are more readily removed using adsorption processes such as through use of activated carbon (28,75) or by oxidation (28). Alum's specificity for higher weight compounds is fortunate since the higher molecular weight organics are the more reactive in forming THMs. In a 1990 review, alum coagulation has been shown to have removal efficiencies of between 50% to 90% of all precursors (69).

The optimization of coagulation involves determining the variables that may influence the process. Numerous studies have demonstrated alum's optimal pH is 5 (78,82,93,96,97). Alum itself serves to lower the pH of water when added. Limits exist for acceptable pH for drinking water based on need for corrosion control and public health. While a lower pH is also preferable to reduce THM formation as previously discussed, raising the pH after treatment does not help reduce THMs during chlorination contact time. Lowering the pH to 5 to optimize coagulation and to destabilize humic substances, then raising it after filtration has not been demonstrated to be a cost-effective or desirable undertaking in view of capital expense and maintenance problems.

Coagulant aids may have the potential to increase the efficiency of the clarification process. While various organic polymers have been used for this purpose, study in this area has been limited. A 1987 study found that polymer coagulant aids did help turbidity removal but not THM precursor removal (98). The possibility that the polymers or contaminants in the polymer products may serve as precursors themselves has been suggested (51,76). Numerous reports of the use of calcium (Ca^{++}) or sodium (Na^{+}) have demonstrated the beneficial effects of cations to aid alum coagulation (79,82,99).

While it could be expected that temperature would influence alum's ability to remove precursors, a 1986 study by Knocke *et al* (64) concluded that it did not.

CHLORINATION POINT: Reductions of TTHMs formed as a result of moving the chlorination point have been reported to reduce THMs by 50% to 62% (83,100). Removal of the precursors to THMs is beneficial only if it precedes the application of chlorine (11,58,91,101). Several plant and distribution system studies have confirmed the advantages of changing the point of chlorination from the raw water ("prechlorination") to clarified water ("postchlorination") (58,102,103).

Post chloination provides the advantages of greatly reduced levels of precursors, minimization of chlorine-precursor contact time (104), and lowered pH of the water (62), all of which reduce THMs in the final product.

Traditionally the pH of calcium carbonate saturation (Langlier Index) has been sought to minimize the corrosiveness of water (105). This meant, for waters of average alkalinity and hardness, using caustic soda (sodium hydroxide) to elevate the pH above 8. As noted above, more THMs are produced with chlorination at higher pH so alternate methods of corrosion control have been sought. Zinc orthophosphate has been shown to be an effective corrosion inhibitor at pH 6.5 to 8.2 (62). The lower pH can be beneficial for reducing TTHMs.

ALTERNATE DISINFECTANTS: Alternate disinfectants to lower TTHMs may be useful either to: 1) replace prechlorination with a different oxidant to oxidize precursors and control biological activity within the treatment plant, or 2) replace the free chlorine residual maintained in drinking water throughout the distribution system for microbiological control.

The EPA published a 1982 project summary on how to study alternate disinfectants to reduce or eliminate THMs in finished drinking water (water having gone through treatment) (106). The main goal was stated to be to reduce disinfection by-products in finished water *"without compromising the microbiological quality of the water"*.

Depending upon the raw water quality, microbiological, biological, taste and odor problems may develop in a treatment plant without the use of a preoxidant (107). Potassium permanganate ($KMnO_4$) has been used successfully as a preoxidant (99,108,109,110). $KMnO_4$ works well with alum (99) because manganese dioxide, resulting from the reduction of $KMnO_4$, can act to adsorb THM precursors and aid in their removal (99,108). $KMnO_4$ is more reactive at higher pH which is an advantage when the raw water pH is high (108). Potassium permanganate, however, is not a strong enough disinfectant for success in maintaining the microbiological quality of water in the distribution system (55,90).

Chlorine dioxide (ClO_2) has been used in drinking water treatment since 1944 (111). ClO_2 has been shown to be effective as both preoxidant (109,112) and postoxidant (55,111,113). While very effective in reducing THM precursors by oxidation and THMs by eliminating a high free chlorine residual, ClO_2 has its disadvantages. Chlorite and chlorate are harmful by-products of the reduction of ClO_2 (109,114) and a dose of <1.0 mg/L must be used to keep these non-THM by-products below limits. Major capital expenditures and training of operators is necessary to implement ClO_2 in a plant not designed for it (55). Current California Department of Health Services regulations for chlorite, chlorate and chlorine dioxide preclude its use in California (29).

Ozone is an oxidant used primarily as a preoxidant followed by another disinfectant in the finished water. Ozone has been shown to aid in precursor removal (102,103). In a 1990 study, Myers concluded, based on cost and effectiveness in reducing THMs, ozone was better than monochloramine which in turn was better than chlorine. However, there are also harmful by-products of ozonation, such as bromate (19,114), formaldehyde and acetaldehyde (57).

Chloramine has been used with success by a number of agencies to reduce THMs (29,55,103,112,115). Switching a plant from chlorination to chloramination is simpler than

implementing ClO_2 or ozone (55,103). Chloramine is formed by adding ammonia to chlorinated water, the resulting desired monochloramine is more stable and does not form THMs as readily as free chlorine (55,57,59,103). It is also a weaker oxidant than chlorine which may make it difficult to meet the disinfection contact times required under new Surface Water Treatment regulations (21,29). Chloramination must be closely monitored to avoid forming undesirable, though unregulated, harmful by-products such as di- and tri-chloramines. Monochloramine is toxic to aquatic life (19,57).

ACTIVATED CARBON: Activated carbon in two forms, powdered or granulated, has been used to remove THM precursors (80,113,116,117,118,119) as well as to remove THMs (90,103,117). Preventing THMs from occurring is more cost-effective than removal in most cases (90,117). While activated carbon may be a useful supplement to chemical coagulation, alone it compares unfavorably to alum's percent removal of precursors. Carbon may be particularly useful for lower molecular weight precursor removal where alum is less efficient (28,75).

ALTERNATE TREATMENTS: Softening with lime has been shown to remove THM precursors as effectively as alum coagulation with certain raw waters (91,115,120). Membrane softening has also been shown to reduce THM formation via precursor removal (121). Removal of aquatic organic

substances has also been reported with anion exchange resins. Fu and Symons reported in 1990 that the use of cation-anion exchange resins after conventional treatment and filtration removed up to 80% of precursors before postchlorination (122).

Removal of THMs after they are formed is another possibility. Activated carbon has been used with success but very high costs and disposal problems make it undesirable. Aeration, or air striping, has been shown to be an effective method to remove THMs based on the compounds' volatilization coefficients from water (103,123) but pose problems for air quality regulations. Another possibility for removal of disinfection by-products has been suggested by Croue and Reckhow, 1989, as destruction with sulfite which would break down the DBPs (124). Further study of by-products produced and chemicals that could be used is necessary before evaluation of the use of chemical reduction of THMs could be complete.

STATEMENT OF THE PROBLEM

The Antelope Valley East Kern Water Agency (AVEK) is one of several agencies receiving water from the California Aqueduct supplied from the Sacramento-San Joaquin Delta. In fact, water for over 20 million Californians and more than half of California's farm irrigation comes from this source (26,29). Numerous surveys of the water quality of the Delta and California Aqueduct have shown that DBP precursors and bromide are significant problems (24,29,125). Treatment practices to make the highest quality drinking water, meeting State and Federal requirements, are of utmost importance to all who use this source.

The complexity of THM formation and control is obvious from the information presented above in the introduction. The interactions between variables are numerous and compounding (and confounding!) At AVEK I have performed several studies where data have been collected and analyzed in a study of variation of nine different parameters: pH levels, oxidant ($KMnO_4$), coagulation aids, activated carbon, rechlorination, chlorination point, raw water quality, off-line raw water storage, and retention time. Success in lowering TTHM concentration has been realized by 1) using zinc orthophosphate for corrosion control instead of raising the pH with sodium hydroxide, 2) using no pre-oxidant or using $KMnO_4$ as a pre-oxidant, 3) optimizing plant maintenance and treatment efficiency, 4) reducing retention

time, 5) using rechlorination to reduce chlorine dose and contact time (126). Constantly changing raw water quality and treatment conditions cause problems in useful and consistent analysis and evaluation of data.

A baseline is needed for comparison to determine whether treatment is optimized for any set of raw water conditions. Without the availability of parallel treatment plants with the capability of providing different treatment regimens, it is difficult to determine whether the treatment is optimum for the raw water quality on any given day.

In addition to the need for a baseline from which to analyze treatments, surrogate parameters are needed for TTHMs. The analysis of TTHMs is time-consuming and costly. Several surrogates have been shown to be indicators for TTHM formation. TOC is perhaps the most utilized of surrogates and has shown to be a good indicator for TTHM formation by numerous researchers (63,64,79,82,98,104,112,117,119). However others have found TOC not to correlate well with TTHMs (11,91,94,127). Perhaps the difference in results reflects the substances comprising the TOC and their varying reactivities for forming TTHMs. The use of ultraviolet (UV) absorbance at 254 nanometers has also met with mixed reviews, some finding good correlation (63,69,70,93,98,104, 128,129) and others poor correlation with TTHMs (11,103,127).

Since bromide has been found to be one of the major factors in TTHM formation, especially in Delta water (24,125,130), its usefulness as a surrogate will be tested in this study.

Developing a model to predict TTHMs based upon one or several variables would provide the framework for treatment optimization and help elucidate the interactions taking place. Several models have been proposed, however, they have been shown to be source specific (15,53,54,61,70, 129,131,132,133,134). The models already developed have been predominantly intended for chlorinating raw water without any other treatment. A good predictive model, specific for the California Aqueduct water undergoing conventional treatment, is needed. From this model, optimization experiments could be evaluated, the reactions would be better understood, and the ultimate control over THM and DBP formation could be sought.

This study attempts to develop a model for predicting TTHM formation undergoing conventional treatment. The parameters which will be evaluated will be pH, temperature, total coliform bacteria density (MPN), NTU, bromide concentration, and treatment parameters singly and multiplicatively. TOC and UV absorbance measurements have been omitted only because the capabilities of the in-house laboratory do not include these analyses. This study is unique in that the data used is empirical data, obtained

from treatment plant samples. This results in varying combinations of variables, unlike the traditional laboratory or pilot plant experiments where one variable is manipulated while others are held constant.

METHODS AND MATERIALS

DATABASE: The samples used for the database were collected beginning July 1988 through October 1991. The samples were collected at least quarterly and sometimes more frequently when special tests were performed. The samples were collected from four different treatment plants, all receiving water from the California Aqueduct in Southern California. All plants use conventional treatment with alum coagulation, sedimentation, and dual media filtration. Three of the plants, Acton (A), Eastside (E), and Quartz Hill (Q) have direct turn-outs from the aqueduct. The Rosamond (Rm) plant receives water through an enclosed 25 mile gravity pipeline from the aqueduct to a 6 million gallon concrete lined raw water reservoir which then supplies the plant.

The Rosamond plant received high quality well water during 1991 and was omitted from the study during that period. The Acton plant did not begin operation until 1991 and only one sample was available for this study. Samples that did not have complete information available were not included.

The water average quality and treatment parameters were measured for the two days preceding and the sample day and are presented in Table 1. The THMs and bromide concentrations were measured on the sample day only. The plant influent (PI) water quality parameters measured on

TABLE 1: DATABASE. Data for variables utilized in statistical calculations and model formation. (Continued next page).

SAMPLES:	DEPENDENT VARIABLES:					INDEPENDENT VARIABLES:						
PLANT/DATE	CL3 ug/L	BDCM ug/L	DBCM ug/L	BR3 ug/L	TTHMs ug/L	PIBRMIDE mg/L	PINTU NTU	PITEMP °C	PIMPN	PIpH	CWRpH	RESIDCL2 mg/L
A. 8/29/91	12	30	56	22	120	0.38	12	24	2400	8.23	7.56	1.0
E. 5/9/89	5	8.6	10	2.0	25.6	0.09	9.5	21	16	8.33	6.97	0.70
E. 9/5/89	1.9	6.5	13	6.9	28.3	0.20	9.3	22	6	7.45	6.60	0.35
E. 3/26/90	2.9	9.6	22	14	48.5	0.28	9.6	17	38	8.10	7.07	0.50
E. 6/19/90	2.9	16	34	29	81.9	0.36	6.5	22	380	8.05	7.48	0.50
E. 8/30/90	7.4	20	35	18	80.4	0.35	1.6	24	2400	8.38	7.38	0.60
E.10/30/90	0.69	2.6	11	17	31.3	0.34	2.5	19	640	8.68	7.37	1.1
E.12/13/90	0.88	3.4	18	44	66.3	0.51	4.8	12	13	8.02	7.18	0.50
E. 6/27/91	8.7	24	40	19	91.7	0.34	12	20	2400	7.82	6.83	0.75
E. 8/29/91	6.0	22	49	24	101	0.39	5.8	23	2400	7.77	6.65	0.55
E. 9/11/91	3.4	12	34	22	71.4	0.35	2.6	23	1400	8.02	6.68	0.55
E.10/10/91	0.42	7.2	25	22	54.6	0.33	5.8	23	2400	7.75	6.62	0.70
Q. 5/9/89	16	10	6.5	<0.5	32.5	0.07	8.6	22	75	8.09	7.04	0.80
Q. 9/5/89	7.6	16	16	4.5	44.1	0.20	5.8	24	25	7.62	7.05	0.40
Q. 3/26/90	8.6	15	20	7.3	50.9	0.28	2.7	17	56	7.80	7.34	0.50
Q. 6/19/90	4.0	15	28	24	71.0	0.37	2.7	21	120	7.85	7.35	0.75
Q. 8/30/90	4.0	11	20	17	52.0	0.36	2.1	24	1230	8.23	7.54	0.55
Q. 9/6/90	5.3	16	22	11	54.3	0.26	3.2	24	2400	7.82	7.42	0.40
Q.10/30/90	1.1	5.4	18	23	47.5	0.32	1.5	19	730	8.56	7.42	0.50
Q.12/13/90	2.6	10	33	28	73.6	0.48	3.5	13	150	8.14	7.34	0.75
Q. 6/27/91	11	30	43	14	98.0	0.39	9.6	20	1600	8.06	7.09	0.35
Q. 8/15/91	10	30	56	14	110	0.44	6.0	22	700	7.88	7.21	0.50
Q. 8/29/91	8.4	25	48	18	99.4	0.32	7.5	23	2400	8.02	7.32	0.50
Q. 9/10/91	2.4	8.1	22	16	48.5	0.36	2.6	23	2400	7.97	7.31	0.80
Q.10/10/91	1.2	9.6	27	26	63.8	0.31	4.0	22	5800	7.81	7.19	0.50
Rm. 7/5/88	20	35	45	16	116	0.32	4.0	24	14	8.41	6.65	1.1
Rm. 5/9/89	21	18	11	<0.5	50.0	0.08	11	23	23	7.79	7.75	2.5
Rm. 9/5/89	7.4	15	19	5.0	46.4	0.20	7.8	25	43	7.79	6.88	1.5
Rm.3/26/90	28	46	44	10	128	0.28	5.9	17	<2.2	7.57	6.83	1.2
Rm.6/20/90	2.8	9.6	19	17	48.4	0.39	3.7	23	60	8.09	6.99	1.3
Rm.8/30/90	6.1	21	39	24	90.1	0.37	2.9	24	400	7.92	7.20	1.9
Rm10/30/90	1.5	6.7	20	22	50.2	0.34	8.3	20	190	8.45	7.12	2.7
Rm12/13/90	2.5	12	33	41	88.5	0.47	2.7	15	23	8.17	7.01	2.2

ABBREVIATIONS: CL3=chloroform. BDCM=bromodichloromethane, DBCM=dibromochloromethane, BR3=bromoform, TTHMs=total trihalomethanes, PIBRMIDE=plant influent bromide concentration, PINTU=plant influent turbidity in nephlometric turbidity units, PITEMP=water temperature in °C, PIMPN=plant influent bacteriological density in Most Probable Number per 100ml, PIpH=plant influent pH, CWRpH=finished water (in Clear Well Reservoir) pH, RESIDCL2=total chlorine residual mg/L in CWR.

TABLE 1 continued: DATABASE. Data for variables utilized in statistical calculations and model formation.

SAMPLES:	INDEPENDENT VARIABLES:											
PLANT/DATE	PICLDOSE mg/L	TWCLDOSE mg/L	PITWDOSE mg/L	PECLDOSE mg/L	TWPEDOSE mg/L	TOTALCL mg/L	ALUM mg/L	ZINC mg/L	KMnO4 mg/L	POLY mg/L	CARBON mg/L	MGD
A. 8/29/91	3.0	0.8	0	0.7	0	4.50	100	0	0	0	0	0.782
E. 5/9/89	0	0	0	0	2.00	2.00	96	0.46	0.64	0	0	3.27
E. 9/5/89	0	0	0	0	2.30	2.30	96	0.48	0.58	0	0	2.70
E. 3/26/90	0	0	0	0	2.00	2.00	84	0.50	0.50	0	0	2.41
E. 6/19/90	0	0	0	0	2.83	2.83	29	0	0.47	2.00	0	3.39
E. 8/30/90	2.48	0	0	0	1.26	3.74	26	0.45	0	2.00	0	4.22
E.10/10/90	0	0	0	0	2.17	2.17	59	0.47	0	0	0	3.25
E.12/13/90	0	0	0	0	1.87	1.87	67	0.48	0	0	0	2.08
E. 6/27/91	2.08	0	0	0	1.80	3.88	82	0.47	0	0	0	2.36
E. 8/29/91	2.23	0	0	0	1.46	3.69	88	0.48	0	0	0	3.01
E. 9/11/91	0	0	0	0	3.05	3.05	85	0.48	0	0	0	2.65
E.10/10/91	0	0	0	0	2.66	2.66	80	0.55	0	0	6	3.15
Q. 5/9/89	0	0	3.39	0.53	0	3.92	81	0.61	0	0	0	22.7
Q. 9/5/89	0	0	2.80	0.80	0	3.60	28	0.50	0	1.63	0	26.7
Q. 3/26/90	0	0	2.40	0.90	0	3.30	43	0.25	0	2.00	0	12.4
Q. 6/19/90	0	0	2.50	1.00	0	3.50	29	0.54	0	1.80	0	25.2
Q. 8/30/90	0	0	2.45	0.50	0	2.95	34	0.55	0	2.30	0	34.7
Q. 9/6/90	0	0	0	0	2.60	2.60	33	0.54	0	2.25	2.0	33.0
Q.10/30/90	0	0	0	0	2.13	2.13	59	0.56	0	0	2.0	26.8
Q.12/13/90	2.50	0	0	1.0	0	3.50	69	0.80	0	0	0	17.4
Q. 6/27/91	3.50	0	0	1.0	0	4.50	125	1.13	0	0	0	12.6
Q. 8/15/91	3.44	0	0	0.33	0	3.77	74	0.50	0	0	0	22.3
Q. 8/29/91	3.67	0	0	0.07	0	3.74	73	0.72	0	0	0	23.6
Q. 9/10/91	0	1.59	0	1.22	0	2.81	77	0	0	0	0	23.5
Q.10/10/91	0	1.90	0	0.86	0	2.76	79	0.49	0	0	3.0	20.3
Rm. 7/5/88	0	0	0	0	4.10	4.10	50	0.50	0.60	0	0	3.69
Rm. 5/9/89	0	0	0	0	4.00	4.00	43	0.55	0.68	2.00	0	4.78
Rm. 9/5/89	0	0	0	0	3.23	3.23	35	0.55	0.27	2.00	0	4.52
Rm.3/26/90	0	0	0	0	3.47	3.47	32	0.50	1.00	2.00	0	3.05
Rm.6/20/90	0	0	0	0	3.15	3.15	32	0.50	0.55	2.00	0	3.86
Rm.8/30/90	2.60	0	0	0	1.93	4.53	32	0.50	0.53	2.00	0	5.16
Rm10/30/90	0	0	0	0	3.20	3.20	60	0.53	1.00	0	0	3.09
Rm12/13/90	0	0	0	0	3.20	3.20	60	0.50	1.10	0	0	2.07

ABBREVIATIONS: The first six variables indicate gaseous chlorine application point, when two points are indicated the dose was split with an unknown proportion at either point. PI=plant influent, TW=treated water,prior to filters, PE=plant effluent, after filters, TOTALCL=total amount of chlorine used, ALUM=liquid alum dose(50%alum), ZINC=zinc orthophosphate dose, KMnO4=potassium permanganate used as a pre-oxidant, POLY=cationic polymer used as a pre-oxidant, POLY=cationic polymer used as a coagulant aid, CARBON=powdered activated carbon, applied at PI, MGD=flow rate in million gallons per day, a relative indication of reaction time.

site were: turbidity in nephelometric turbidity units (PINTU), pH (PIpH) and temperature in °C (PITEMP). The finished drinking water quality in the clear well reservoir(CWR) was measured on site for total residual chlorine in mg/L (RESIDCL2) and pH (CWRpH). The treatment variables recorded were also averaged for the two days preceding and sample day. The flow rate in million gallons per day (MGD) relates directly to reaction time based upon the capacity of each plant. The treatment variables included the liquid alum dose in mg/L (ALUM), the cationic polymer in mg/L (POLY), powdered activated carbon in mg/L (CARBON) and the mg/L of the pre-oxidant potassium permanganate ($KMnO_4$). The $KMnO_4$ was applied to the influent of the raw water reservoir at the Rosamond plant and at the plant influent to the Eastside plant. Activated Carbon was added at the plant influent if used. The application points and doses of chlorine used (mg/L) were also recorded (see Table 1) and the total mg/L chlorine applied calculated (TOTALCL).

CHEMICAL ANALYSIS: The laboratory analyses performed on the samples were the total trihalomethanes (TTHMs) in the CWR and plant influent bromide concentration in mg/L (PIBRMIDE). The THMs were analyzed by EPA method 502.2 (Gas Chromatograph, purge and trap, Hall detector, Restek 502.2 capillary column). The bromide was analyzed by EPA method 300.0 (suppressed ion chromatography). Standard quality

control practices for the analytical methods included quality control check samples, 10-20% duplicate samples, spiked recovery samples, calibration curves and detection limit calculations for each analysis date. The calculated detection limit was consistently below the DLR (detection limit for the purposes of reporting) of 0.5 ug/l for each of the four trihalomethanes. The detection limit for bromide was $\leq$ 0.01 mg/L.

STATISTICAL ANALYSIS: Accumulated data was entered into the computer programs: Quatro Pro spreadsheet (Borland International, Inc., Scotts Valley, CA) and SPSS/PC+ Studentware statistical package (SPSS, Inc., Chicago, IL). Quatro Pro was utilized to graph data, sort data, and perform regression analyses. The SPSS program performed the more detailed statistics used to attempt to build a model to predict TTHMs (dependent variable) from the various independent variables. A replication of the Quatro Pro spreadsheet presents the data used in this study in Table 1. The dependent and independent variables tested are labeled as such. On Table 1, the THMs are expressed as ug/L.

The SPSS regression analysis program provides the correlation coefficient (R) indicating the goodness of fit ($\pm$1 being perfect linear correlation between the dependent and independent variables). The output of the SPSS regression analysis is given in Table 2. The regression output includes the correlation coefficient (R), the

TABLE 2: SPSS METHOD DISPLAY. Multiple regression analysis output.

Equation Number 1 Dependent Variable.. TOTAL

Variable(s) Entered on Step Number
1.. PIBRMIDE
2.. TOTALCL
3.. PICLDOSE

Multiple R	.90041
R Square	.81073
Adjusted R Square	.76342
Standard Error	10.99772

Analysis of Variance

	DF	Sum of Squares	Mean Square
Regression	3	6217.13217	2072.37739
Residual	12	1451.39788	120.94982

F = 17.13419 Sig F = .0001

Variables in the Equation

Variable	B	SE B	95% Confdnce Intrvl B	
PIBRMIDE	104.244903	30.637905	37.490650	170.9992157
TOTALCL	8.110107	5.881208	-4.703943	20.924157
PICLDOSE	7.416394	2.726168	1.476584	13.356204
(Constant)	-1.350506	23.356552	-52.240057	49.539044

Variable	Beta	T	Sig T
PIBRMIDE	.485447	3.402	.0052
TOTALCL	.232687	1.379	.1931
PICLDOSE	.486958	2.720	.0186
(Constant)		-.058	.9548

constant (C) and slope (B) for each variable. This information is used to compute the best fit of the data or least squares line:

equation 8:

$$y = C + Bx$$

where: y = dependent variable,
x = independent variable,
other terms are identified above.

Information is provided to evaluate the regression analysis such as the standard error of estimates of R, the slope of each variable (SE B), and the 95% confidence intervals for the slope. If the range of the confidence interval of the slope includes zero, the null hypothesis (there is no relationship between x and y) cannot be rejected, therefore no linear relationship exists between the variables (slope = 0). Additional information is the F value which needs to exceed the significant F (Sig F) to reject the null hypothesis, the larger the F value the better the linear relationship. The *t* statistic is also calculated and the significant *t* (Sig *t*) for two-tailed significance is given. As in the F value, the *t* must exceed the Sig *t* to reject the null hypothesis.

MODEL FORMATION: Model formation began with the examination of the TTHMs and individual THMs in *u*g/L, *u*moles/L, and *u*g C/L (*u*g carbon/L). The three different

manners to express THMs were used to examine any differences in species distributions. Graphs and regression analyses were used to look for relationships and/or trends.

Quatro Pro was used to prepare graphs and calculate correlation coefficients for each individual independent variable paired with each dependent variable. The TTHMs and individual THMs were expressed as *u*g/L, *u*moles/L or *u*g C/L. Significant relationships were sought. All independent variables with correlation coefficients (R) greater than absolute 0.20 were chosen for further testing and all others were discounted.

The variables with R greater than absolute 0.20 were run on the SPSS regression program for a more complete statistical profile. The F statistic, 95% confidence interval for the slope and *t* statistic were examined. If the null hypothesis was accepted under any condition the variable was dropped from further inclusion in model development. Since the model will predict TTHMs, independent variables that survived the above tests with individual THMs provided useful and interesting information, but were not used in model development.

Once the significant independent variables were identified, they were entered into multiple regression analysis with every possible combination of independent variables paired with the dependent variables *u*g/L TTHMs, *u*moles/L TTHMs or *u*g C/L TTHMs. The possibility that the

data from the different plants might differentially influence the results was considered, so calculations were also performed as above with each of three plants separately. Acton was not considered separately due to lack of data.

The equations were then examined using Quatro Pro graphs and regression analysis of the predicted values versus the measured values. The SPSS residuals calculation was also used to test the models. The residual value is the difference between the predicted value and the measured value of the dependent variable. If the model is a perfect fit, the residual values are all zero. If it is a poor fit residual values are large. Ninety-five percent of the standardized residuals (the residual value divided by an estimate of its standard deviation) should fall between -2 and +2 for a normal distribution. The standard deviation for the residuals was also considered. Scatterplots of the residuals were examined for any patterns that would indicate the need for data transformation. If the variance appears random the linear model is probably a good fit, if there is a pattern to the variance perhaps transformation (log, square root, etc.) of any of the variables may be called for.

The final models were chosen based on their predictive value as measured by the residuals and standard deviation of residuals. The predicted TTHMs were calculated and plotted

against the measured TTHMs to visually examine the models. The models were then tested against measured values collected at the four plants in 1992 and not included in the database. Accuracy of prediction was judged to be acceptable if it was within ± 20% of the measured value. This range is based upon the EPA acceptability of measurement accuracy for the THM analytical methods.

The suitability of using the most significant independent variables as surrogates for TTHMs was evaluated. The ability of the sole independent variables to predict TTHMs was examined.

RESULTS

The first step was to examine all data and look for relationships. The relationship between TTHMs and individual THMs expressed as *u*g/L, *u*moles/L or *u*g C/L is illustrated in Figures 1, 2 and 3. The graphs were plotted after the data was sorted in ascending order for TTHMs in *u*g/L and every 3 data points were averaged such that the 33 samples are represented by 11 points. All data on the following graphs that include all of the database were prepared in the same manner. All samples, not averages, were used in statistical calculations.

Figure 1 demonstrates that the manner of expression for the TTHMs is not significant. In fact, the R calculated for each possible pairing of these variables show a very close linear relationship with values of 0.98 to 1.0, all strongly rejecting the null hypothesis of no relationship.

A different relationship is seen in Figures 2 and 3 when TTHMs were paired with individual THMs. The graphs illustrate the values in *u*g/L (Figure 2) or *u*moles/L (Figure 3) only, since the relationship of *u*g C/L is nearly identical to that of *u*moles/L seen in Table 3. Table 3 gives the statistics generated for pairing the TTHMs with individual THMs. In *u*g/L, *u*moles/L or *u*g C/L, all slopes for the equations that rejected the null hypothesis are positive. Table 3 shows the strongest relationships between dibromochloromethane (DBCM) and bromodichloromethane (BDCM)

FIGURE 1: TTHMs expressed as ug/L, umoles/L and ug C/L. Averages plotted.

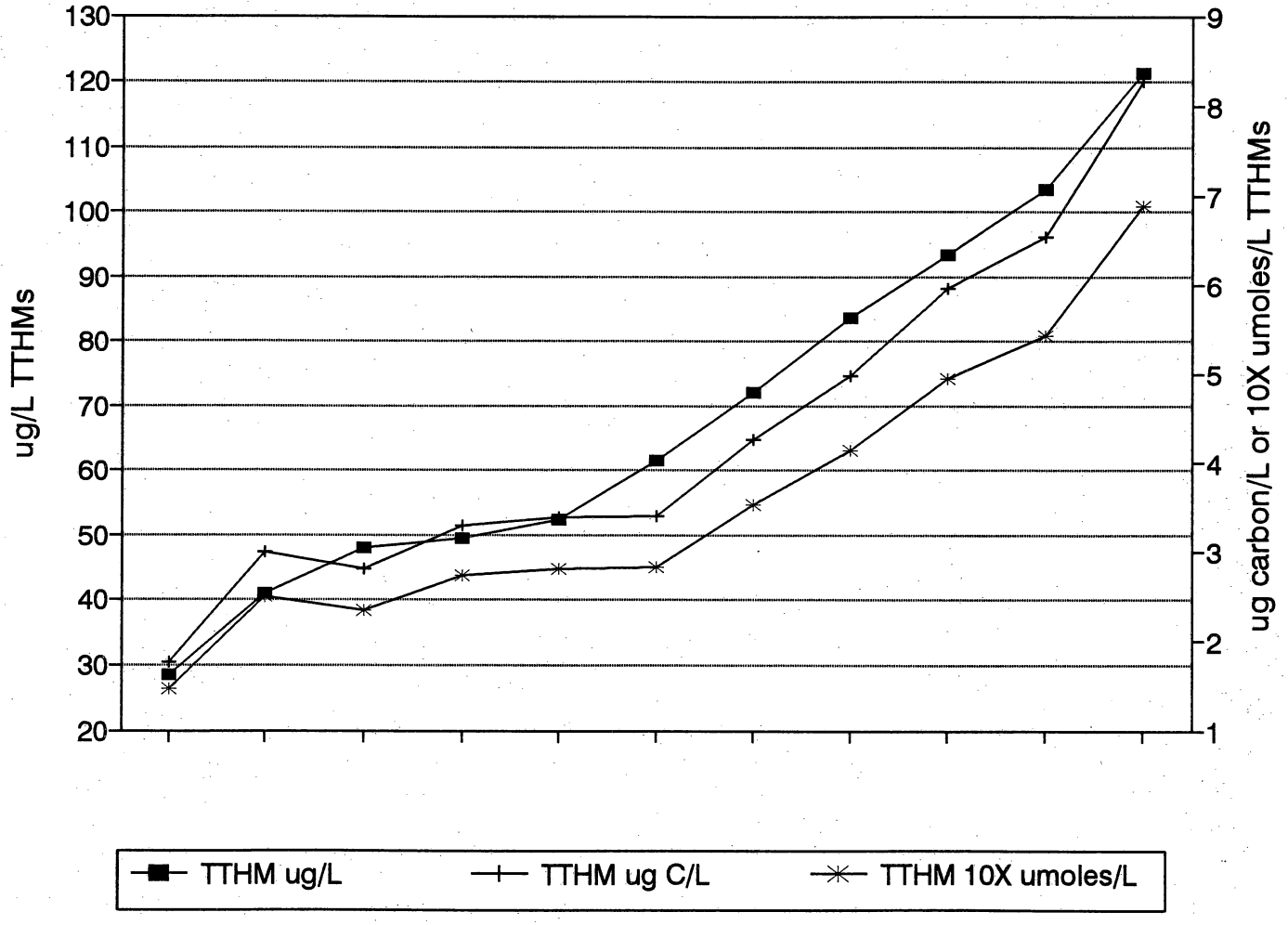


FIGURE 2: THMs and TTHMs as ug/L.
Averages plotted.

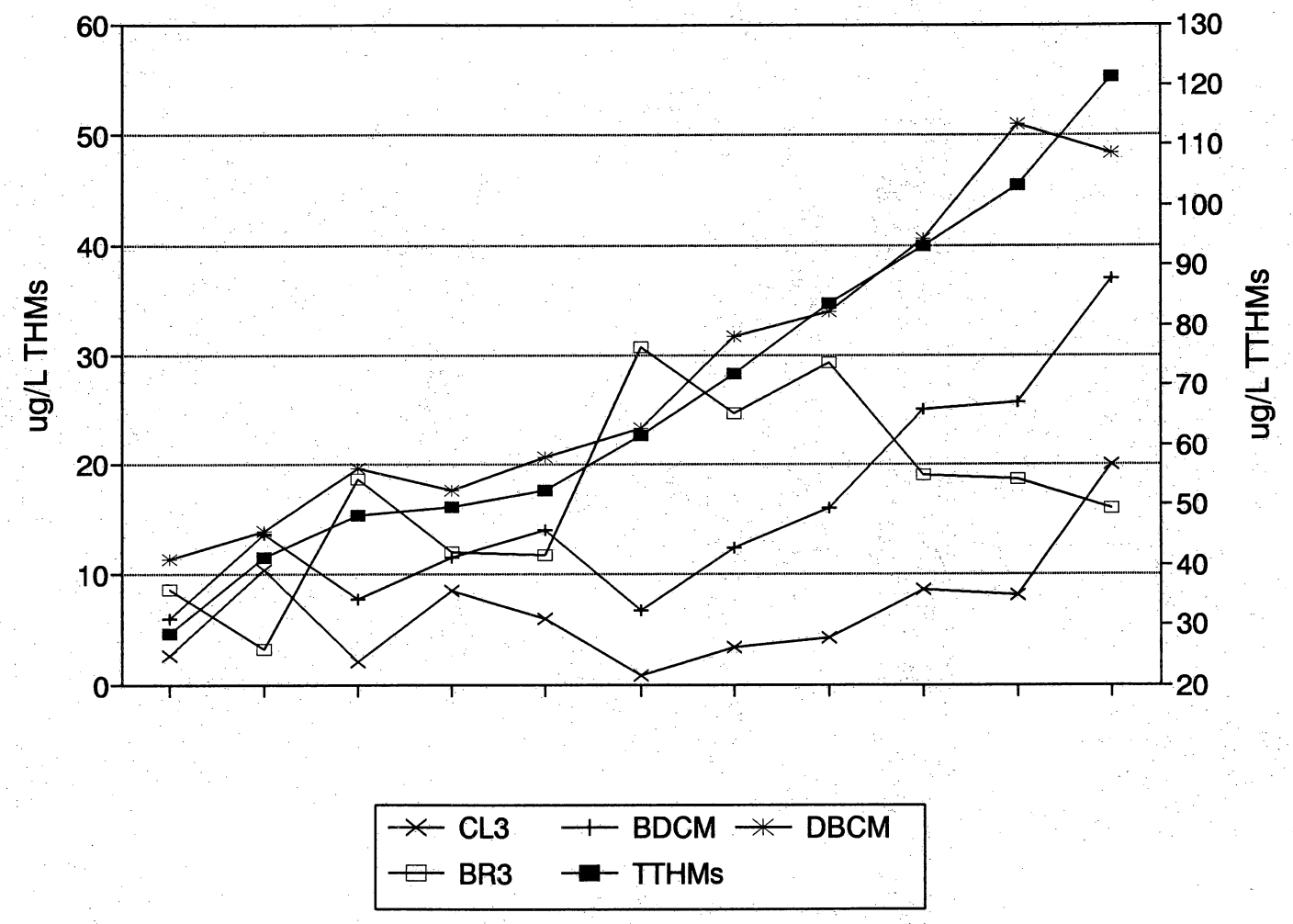


FIGURE 3: THMs and TTHMs as umoles/L.
Averages plotted.

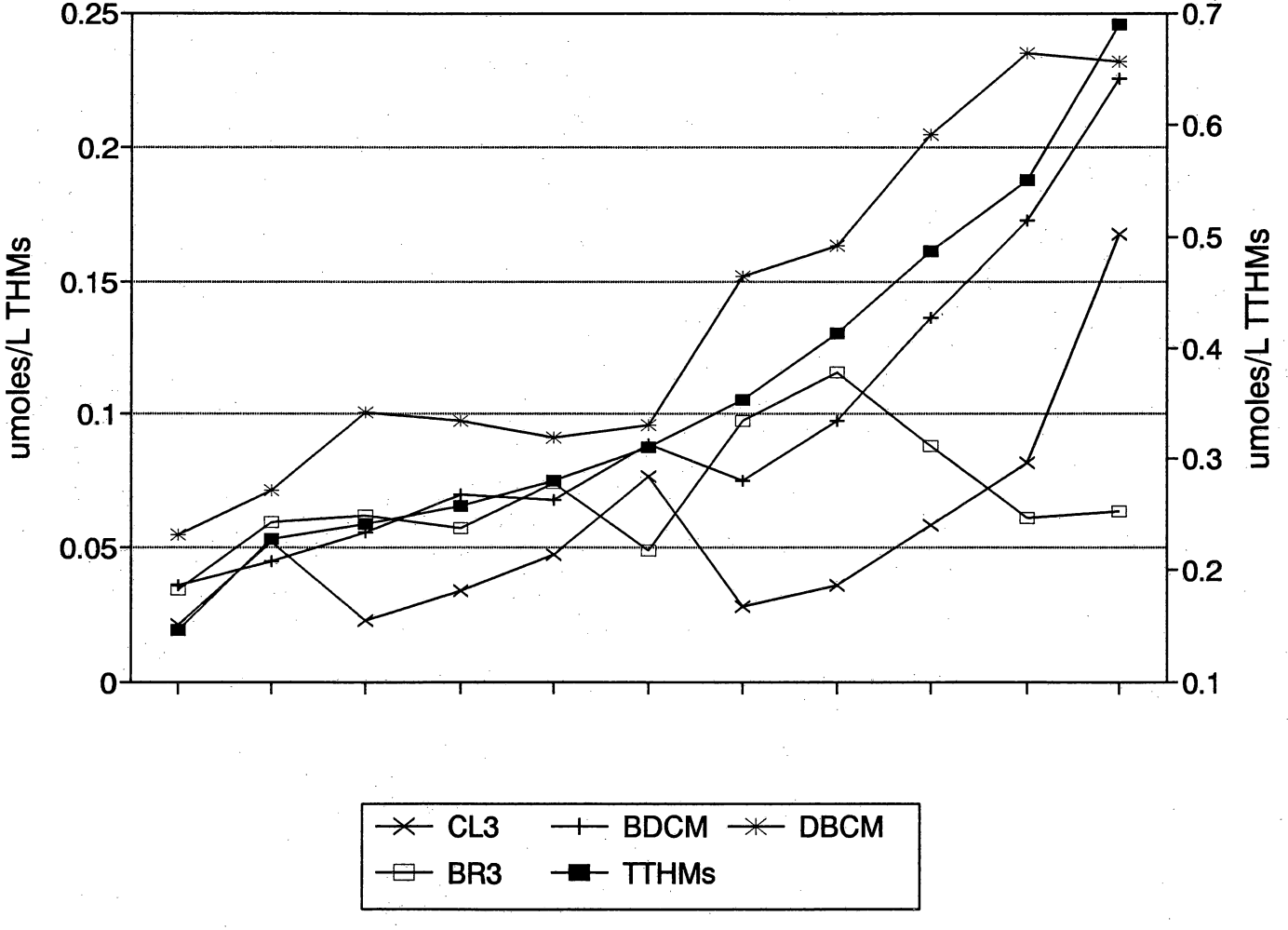


TABLE 3: REGRESSION ANALYSIS. THM vs TTHMs or THM vs THM.

Regression analysis results for individual THMs paired with TTHMs, expressed as mass concentration (ug/L), molar concentration (umoles/L), carbon concentration (ug C/L).

	CL3	BDCM	DBCM	BR3
TOTAL THM ug/L null hypothesis	R = 0.480 rejected	R = 0.848 rejected	R = 0.949 rejected	R = 0.355 rejected
MTOTAL THM umoles/L null hypothesis	R = 0.649 rejected	R = 0.934 rejected	R = 0.901 rejected	R = 0.164 ACCEPTED
CTOTAL THM ug C/L null hypothesis	R = 0.646 rejected	R = 0.932 rejected	R = 0.903 rejected	R = 0.169 ACCEPTED

Regression analysis results for paired individual THMs. Expression as mass concentration, molar concentration, or carbon concentration is not significant as only one compound is involved.

	CL3	BDCM	DBCM	BR3
CL3 null hypothesis		R = 0.795 rejected	R = 0.300 ACCEPTED	R = -0.486 rejected
BDCM null hypothesis	R = 0.795 rejected		R = 0.769 rejected	R = 0.170 ACCEPTED
DBCM null hypothesis	R = 0.300 ACCEPTED	R = 0.769 rejected		R = 0.336 ACCEPTED
BR3 null hypothesis	R = -0.486 rejected	R = 0.170 ACCEPTED	R = 0.336 ACCEPTED	

Null hypothesis:

ACCEPTED = 95% confidence, no linear relationship exists between the variables.

rejected = 95% confidence, a linear relationship exists between the variables.

contributing to TTHMs which remain fairly constant in all three conditions. Chloroform (CL3) has a weaker relationship with TTHMs when considering the mass concentrations, but becomes stronger when looking at *u*moles/L or *u*g C/L. Bromoform (BR3) tends toward the opposite direction, so that a slight relationship with TTHMs when considering mass becomes weaker when considering *u*moles/L or *u*g C/L and the null hypothesis cannot be rejected.

The relationships that exist between the individual THMs is also demonstrated on Table 3. CL3 has a positive linear relationship with BDCM and an inverse or negative relationship (slope) with BR3. The only other linear relationship is a positive one between DBCM and BDCM.

Correlation coefficients were computed between all independent and dependent variables. A correlation table for all possible combinations of variables was prepared, as were scatterplots of data to look for trends. TTHMs were tested separately as *u*g/L, *u*moles/L and *u*g C/L, but this is unnecessary for the individual THMs since the three different ways of expression all represent the same quantity when only one compound is involved.

The individual THMs and TTHMs as dependent variables in relation to the three strongest independent variables is shown in Table 4 and illustrated by Figures 4, 5 and 6. Figures 4 and 5 illustrate the independent variables

PIBRMIDE and PICLDOSE in relation to the THMs expressed as *u*g/L since these were the stronger R values (Table 4). Figure 6 plots the *u*moles/L THMs versus the TOTALCL since this relationship exhibited a slightly stronger R. All slopes of the correlations were positive except for a negative slope representing the inverse correlation between CL3 and PIBRMIDE. The only chlorine application point that had a clear-cut relationship with the dependent variables was the plant influent, Table 4, Figure 5. The other relationships between the dependent and independent variables with R greater than absolute 0.20 that survived the tests for accepting the null hypothesis were PINTU and PITEMP with BR3 (R = 0.37 and R = 0.45 respectively, both with negative slopes).

Similar data manipulations were performed with each of three of the plants treated separately. The Rosamond plant data yielded no relationships between the independent variables and TTHMs (tested as *u*g/L, *u*moles/L and *u*g C/L). In fact only two correlations survived the tests for the null hypothesis: PIBRMIDE with BR3 (R=0.917) and PINTU with BR3 (R=0.724). The Eastside and Quartz Hill databases yielded more correlations greater than absolute 0.20 which also survived the tests for accepting the null hypothesis. Table 5 shows the correlations found. Since the correlations and regression statistics were very nearly

TABLE 4: REGRESSION ANALYSIS.
THM or TTHMS vs Independent Variables.

Regression analysis results for TTHMs and individual THMs as dependent variables paired with the strongest independent variables found.

	INDEPENDENT:		
DEPENDENT:	PIBRMIDE	PICLDOSE	TOTALCL
TOTAL THM ug/L	R = 0.509	R = 0.616	R = 0.624
null hypothesis	rejected	rejected	rejected
MTOTAL THM umoles/L	R = 0.340	R = 0.584	R = 0.686
null hypothesis	ACCEPTED	rejected	rejected
CTOTAL THM ug C/L	R = 0.344	R = 0.585	R = 0.685
null hypothesis	ACCEPTED	rejected	rejected
CL3	R = -0.373	R = 0.143	R = 0.593
null hypothesis	rejected	rejected	rejected
BDCM	R = 0.060	R = 0.506	R = 0.699
null hypothesis	rejected	rejected	rejected
DBCM	R = 0.542	R = 0.740	R = 0.597
null hypothesis	rejected	rejected	rejected
BR3	R = 0.853	R = 0.123	R = 0.137
null hypothesis	rejected	ACCEPTED	ACCEPTED

Null hypothesis:

ACCEPTED = 95% confidence, no linear relationship exists between the variables.

rejected = 95% confidence, a linear relationship exists between the variables.

FIGURE 4: THMs and TTHMs vs Bromide Concentration. Averages plotted.

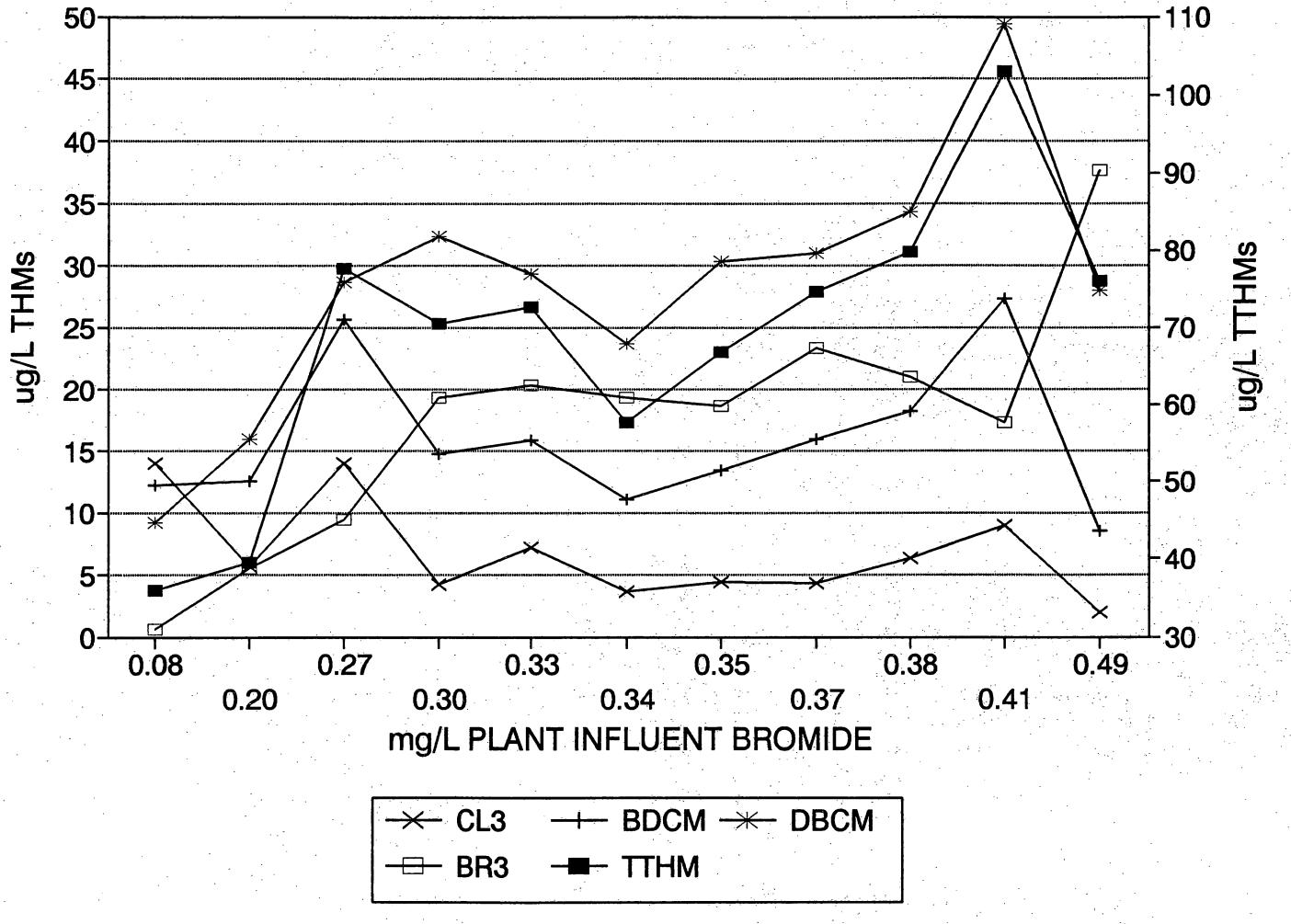


FIGURE 5: THMs and TTHMs vs
PI Chlorine Dose. Averages plotted.

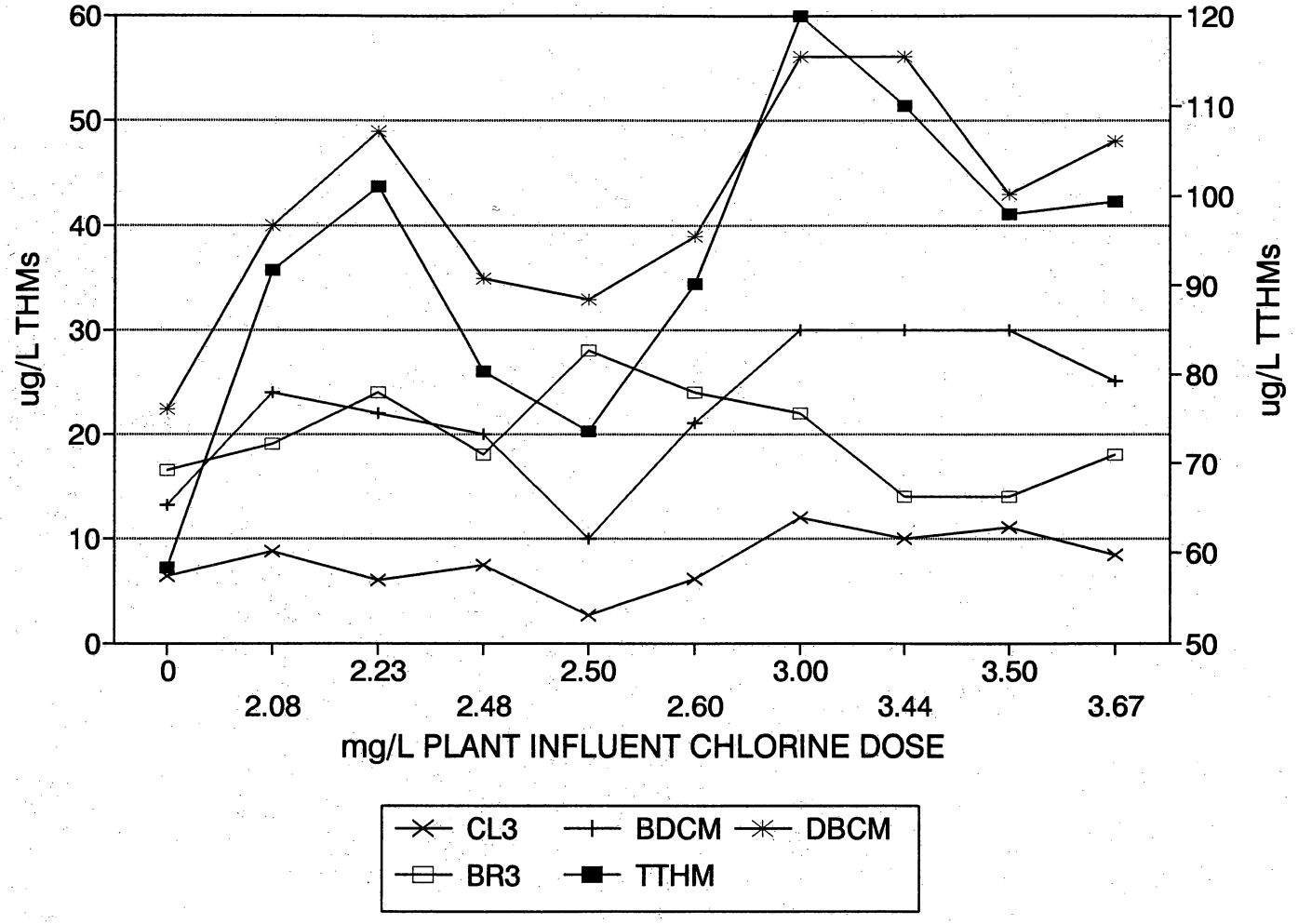


FIGURE 6: THMs and TTHMs vs Total Chlorine Dose. Averages plotted.

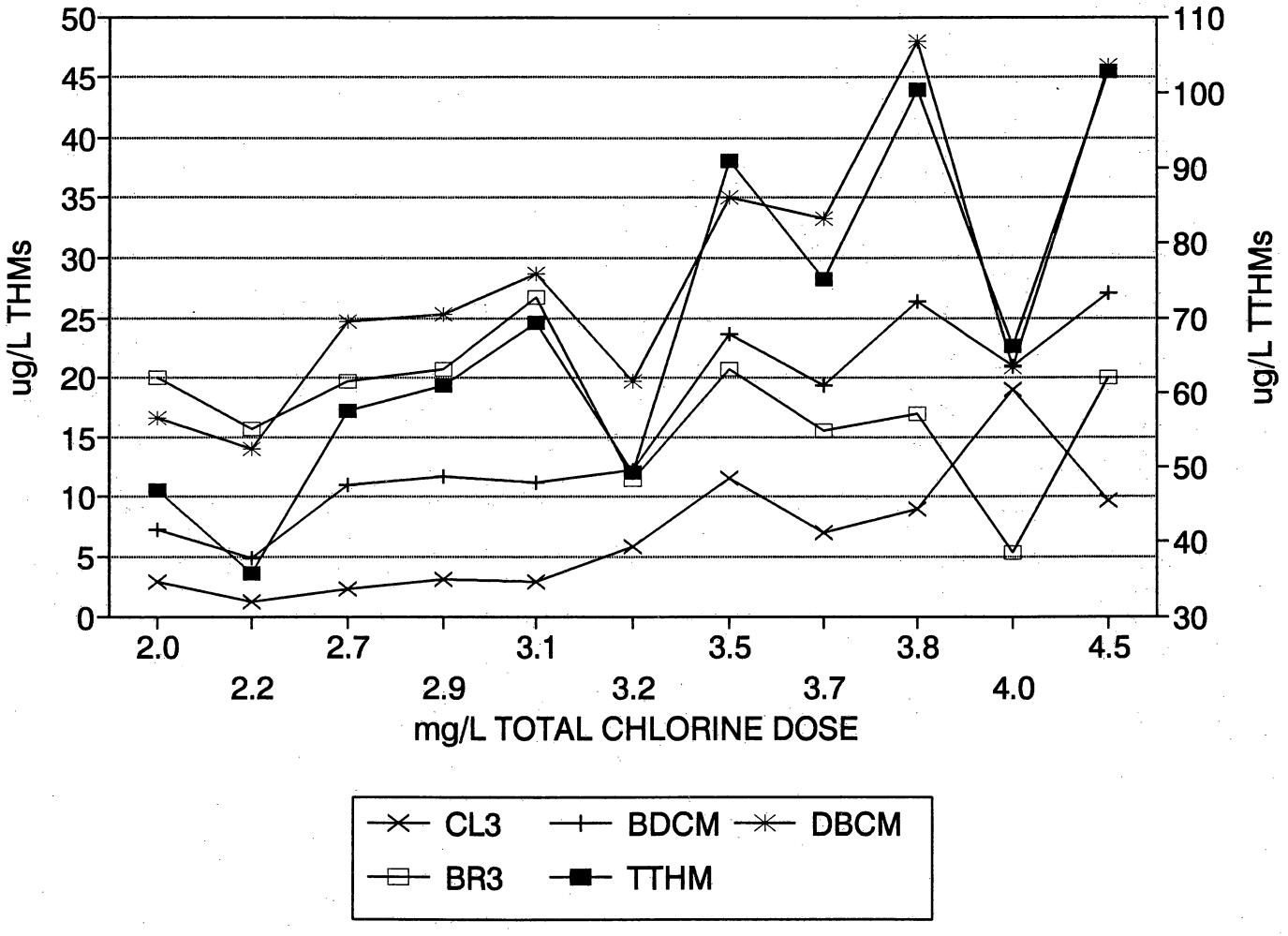


TABLE 5: REGRESSION ANALYSIS. Eastside and Quartz Hill: THMs or TTHMs vs Independent Variables.

R values given where the null hypothesis was rejected. All correlations have a positive slope. Data was separated into individual plant databases.

EASTSIDE DATABASE

DEPENDENT:	INDEPENDENT: PIBRMIDE	PICLDOSE	TOTALCL	PIMPN
TOTAL THM ug/L	R = 0.645	R = 0.700	R = 0.810	R = 0.662
MTOTAL THM umoles/L		R = 0.770	R = 0.868	R = 0.693
CTOTAL THM ug C/L		R = 0.769	R = 0.866	R = 0.693
CL3		R = 0.844	R = 0.773	
BDCM		R = 0.848	R = 0.915	
DBCM		R = 0.728	R = 0.886	
BR3	R = 0.941			

QUARTZ HILL DATABASE

DEPENDENT:	INDEPENDENT: PIBRMIDE	PICLDOSE	TOTALCL	PINTU
TOTAL THM ug/L	R = 0.652	R = 0.905		
MTOTAL THM umoles/L		R = 0.920	R = 0.633	
CTOTAL THM ug C/L		R = 0.920	R = 0.630	
CL3			R = 0.758	R = 0.810
BDCM		R = 0.788	R = 0.705	R = 0.653
DBCM	R = 0.680	R = 0.894		
BR3	R = 0.746			

identical when considering umoles/L and ug C/L, only umoles/L was used in further model development.

To attempt to form an Eastside predictive model for TTHMs the independent variables PIBRMIDE (mg/L), PICLDOSE (mg/L), TOTALCl (mg/L), and PIMPN were entered into regression analysis in all possible combinations of 2, 3 and 4 independent variables and as ug/L TTHMs or umoles/L TTHMs for the dependent variable. Four equations for ug/L TTHMs yielded R >0.9 and the residuals and residual scatterplots were examined before determining the best equation (R=0.941):

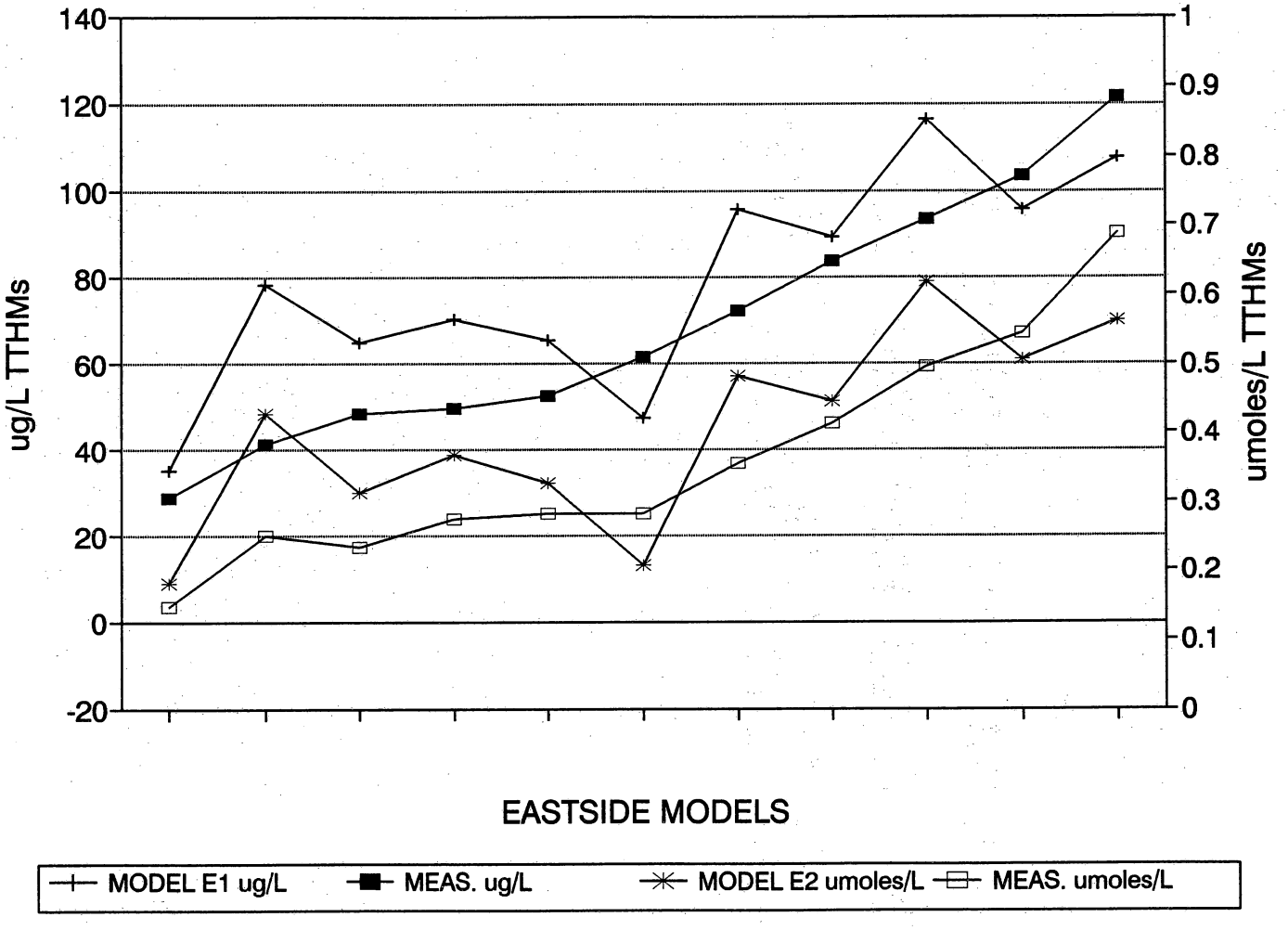
Model E1: uug/L TTHMS = -60.9712+33.6312(TOTALCL)+
120.4933(PIBRMIDE) +
0.4793(PICLDOSE) - 0.007290(PIMPN)

Three equations with R >0.9 were tested for residuals and the best equation for umoles TTHM was found to be (R=0.942):

Model E2: umoles/L TTHMs = -0.29999 + 0.1830(TOTALCL) +
0.4579(PIBRMIDE) +
0.008067(PICLDOSE) -
4.1878×10^{-5}(PIMPN)

The F values and residual data were nearly identical for both equations. The measured and predicted TTHMs using these equations are illustrated in Figure 7.

FIGURE 7: Measured vs Predicted TTHMs
by E1 and E2. Averages plotted.



The Quartz Hill data yielded similar significant independent variables as Eastside with the exception of PIMPN for which the null hypothesis could not be rejected with 95% confidence (Table 5). The three variables tested for inclusion into an equation for TTHMs were: PIBRMIDE, PICLDOSE, TOTALCL. Every possible combination was tested with all but one pair (PIBRMIDE, TOTALCL) yielding R >0.90 for either *u*g/L or *u*moles/L TTHMs. After examining the residuals and scatterplots it was determined the following were the best equations:

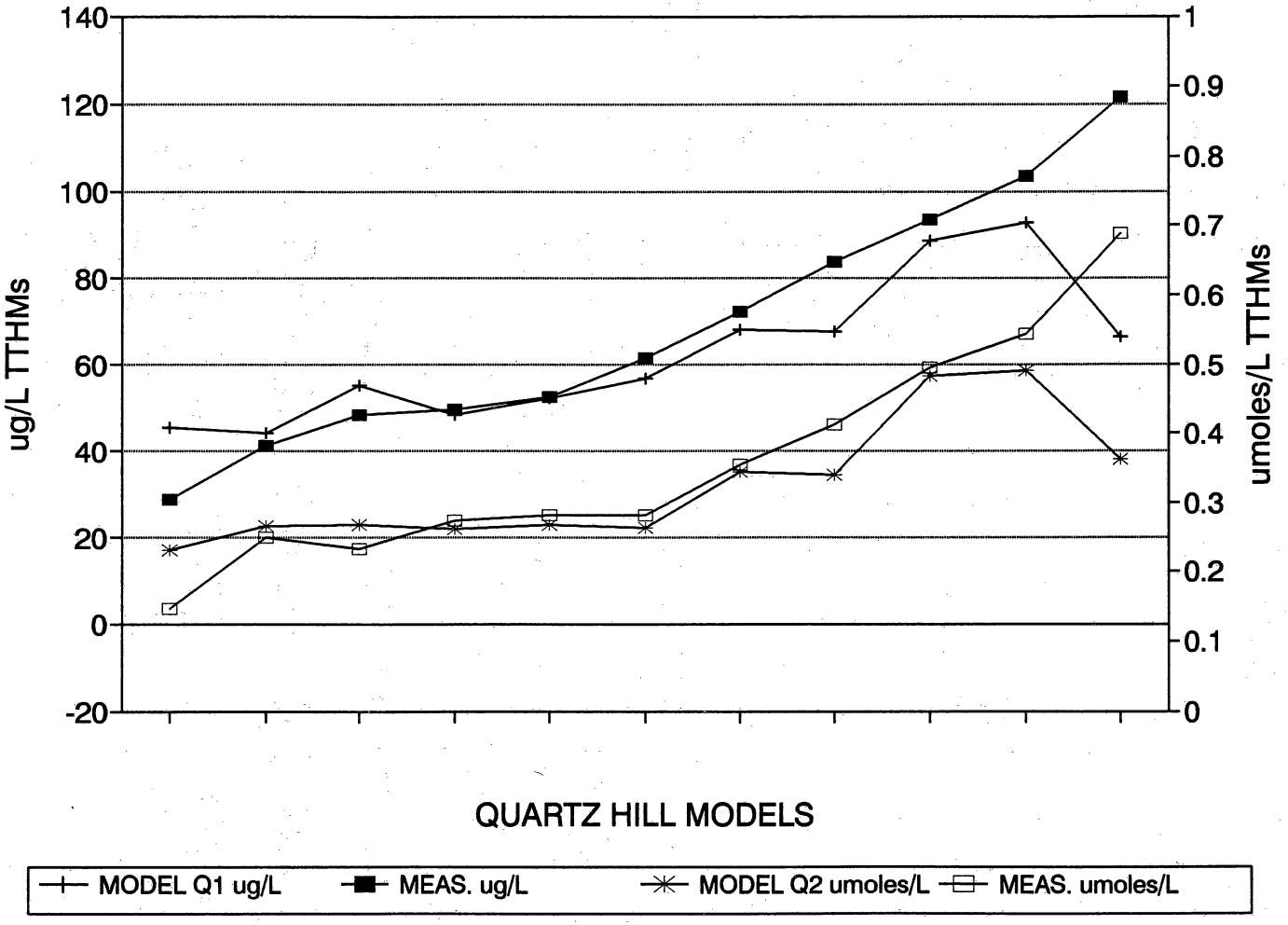
Model Q1: *u*g/L TTHMs = 30.3423 + 1.1938(TOTALCL) + 60.3345 (PIBRMIDE)+ 11.2827 (PICLDOSE)

Model Q2: *u*moles/L TTHMs = 0.1416 + 0.02885 (TOTALCL) + 0.1335(PIBRMIDE) + 0.06126(PICLDOSE)

The R for the first equation is 0.930, for the second R = 0.926. The F tests and residual statistics were very similar for both equations. Figure 8 shows the relationship between measured TTHMs and the TTHMs predicted by the above equations.

A predictive model based on all data in the database was then attempted. Table 4 shows the three independent variables found to have a linear relationship (the null hypothesis was rejected) with TTHMs for all data. Every

FIGURE 8: Measured vs Predicted TTHMs
by Q1 and Q2. Averages plotted,



possible combination of the variables was entered into regression analysis. The final models for all data in the database are:

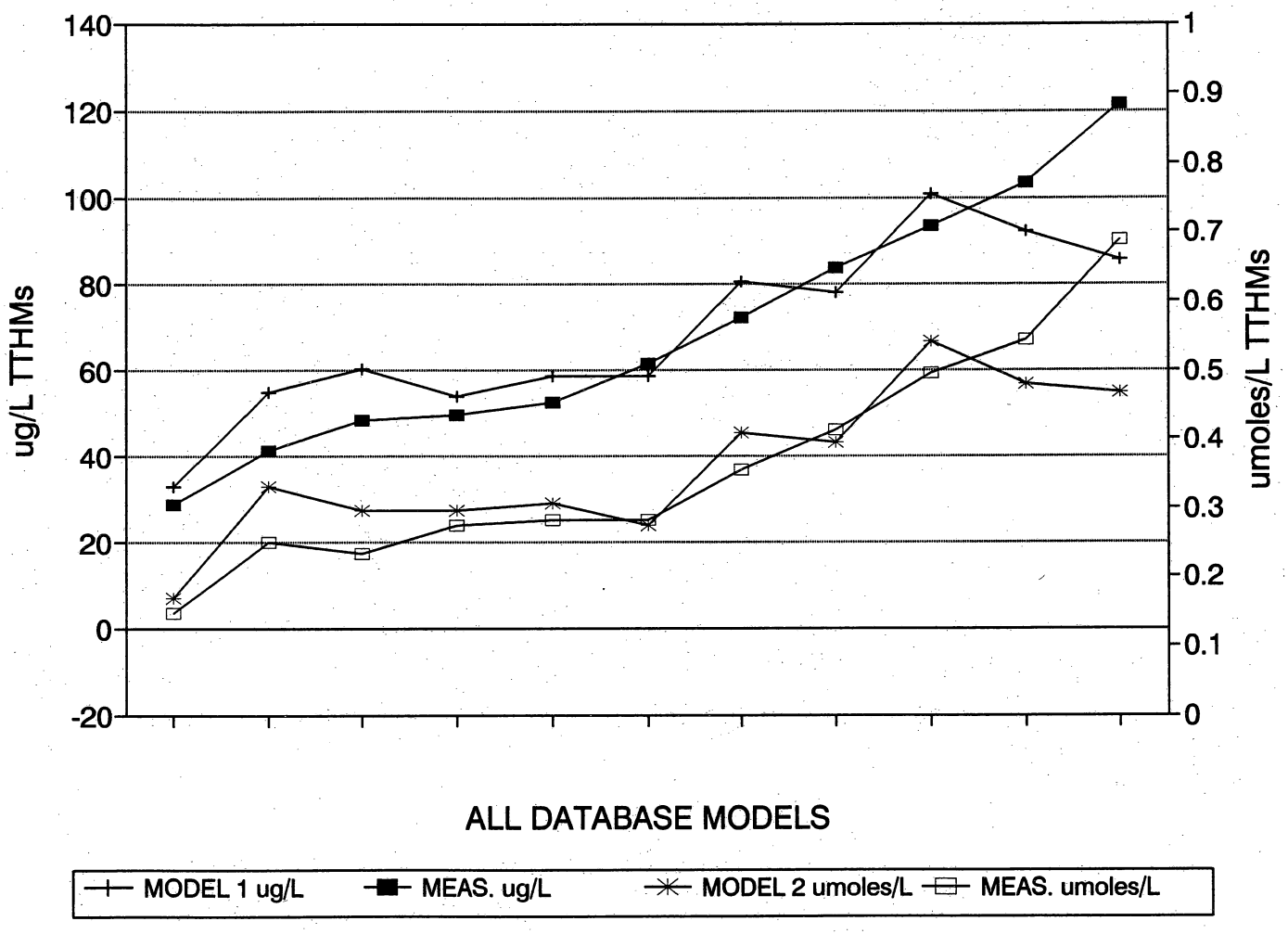
Model 1: ug/L TTHMs = -32.8234 + 19.3378 (TOTALCL) + 114.6749(PIBRMIDE) + 2.9133(PICLDOSE)

Model 2: umoles/L TTHMs = -0.1871 + 0.1268 (TOTALCL) + 0.3962(PIBRMIDE) + 0.01325(PICLDOSE)

The first equation R = 0.790, the second equation has a slightly weaker linear relationship with and R = 0.754. The predicted versus measured data for the above equations is shown in Figure 9.

Examination of the fit of all six models on each sample in the entire database found the two Quartz Hill models had the best fit for the most samples, having the smallest residual for 16 of the 33 samples, 9 of the 16 were from the 13 Quartz Hill plant samples. The Eastside models were next with 10 of the smallest residuals, 6 of which were from the Eastside plant samples. When a model fit the data best in ug/L TTHMs, the same model for umoles/L TTHMs was also the best fit (i.e. when Q1 was best for a sample, so was Q2). A slight pattern was apparent; the Models 1 and 2 were

FIGURE 9: Measured vs Predicted TTHMs
by Models 1 and 2. Averages plotted.



generally better predictors for lower TTHMs and the E1 and E2 models were best for the highest TTHMs.

The Q models were the best overall predictors for the samples in the database. The Q2 model predicted with ± 20% of the measured values in 70% of the database and Q1 predicted as well for 1 less datapoint (67%). Models 1 and 2 predicted within ± 20% for 55% of the 33 samples. E2 was only as close for 42% of the database while E1 predicted within ± 20% for just 21% of the database.

The models were tested against 1992 data for predictive accuracy on data not included in the model formation. Table 6 gives the new raw data for the 18 samples. Figures 10 and 11 illustrate the fit of the predicted values to actual TTHMs. The residuals showed the E1 and E2 models were closest for the higher measured TTHMs, but were best for only 5 and 3 samples respectively. Model 1 was best for 9 samples and Model 2 for 8, both predicting better for TTHMs values in the mid-range. Q1 predicted closest for 4 samples including the 2 lowest TTHMs. Q2 performed better than Q1 but showed a similar trend in having the lowest residuals for 7 values, all in the lower range of TTHM values.

Model 1 yielded predicted TTHMs within ± 20% of the measured values in 11 of the 18 new samples (61%), one sample more than Model 2 (56%). The Model 1 missed the two highest TTHMs, 113 and 140 ug/L by 26% and 36% respectively. Models Q1 and Q2 predicted within ± 20% for 44%, or 8, of

TABLE 6: 1992 DATA.

Raw data for 1992 samples. These samples were not included in the database employed for model development. This new data was used to validate the models developed.

PLANT/DATE	TOTALCL	PICLDOSE	PIBRMIDE	PIMPN	MEASURED ug/L TTHMs	MEASURED umoles/L MTTHMs
Q. 1/23/92	2.33	-	0.45	130	60.0	0.264
E. 1/23/92	1.02	-	0.27	30	47.8	0.213
A. 1/23/92	2.40	1.46	0.46	4	63.9	0.310
Rm. 4/9/92	3.70	-	0.50	<2	81.0	0.392
Q. 4/9/92	3.69	-	0.47	4	91.7	0.466
E. 4/9/92	3.22	-	0.48	30	70.4	0.339
A. 4/9/92	3.40	2.07	0.44	4	139.6	0.707
Q. 5/28/92	2.70	-	0.35	5000	66.1	0.341
Rm. 7/30/92	3.29	-	0.34	1400	100.0	0.534
Q. 7/30/92	3.56	-	0.34	4000	78.2	0.404
E. 7/30/92	2.79	-	0.34	5000	87.9	0.442
A. 7/30/92	4.00	-	0.34	5000	113.3	0.602
Rm. 11/5/92	2.90	-	0.47	11	87.5	0.400
Q. 11/5/92	2.63	-	0.47	13	65.9	0.287
E. 11/5/92	2.90	-	0.50	24	73.0	0.322
A. 11/5/92	3.50	-	0.48	23	103.4	0.478
Rm. 12/22/92	3.55	-	0.38	13	80.4	0.385
A. 12/22/92	2.30	-	0.35	8	67.8	0.314

FIGURE 10: 1992 Measured vs Predicted
TTHMs as ug/L. All new data plotted.

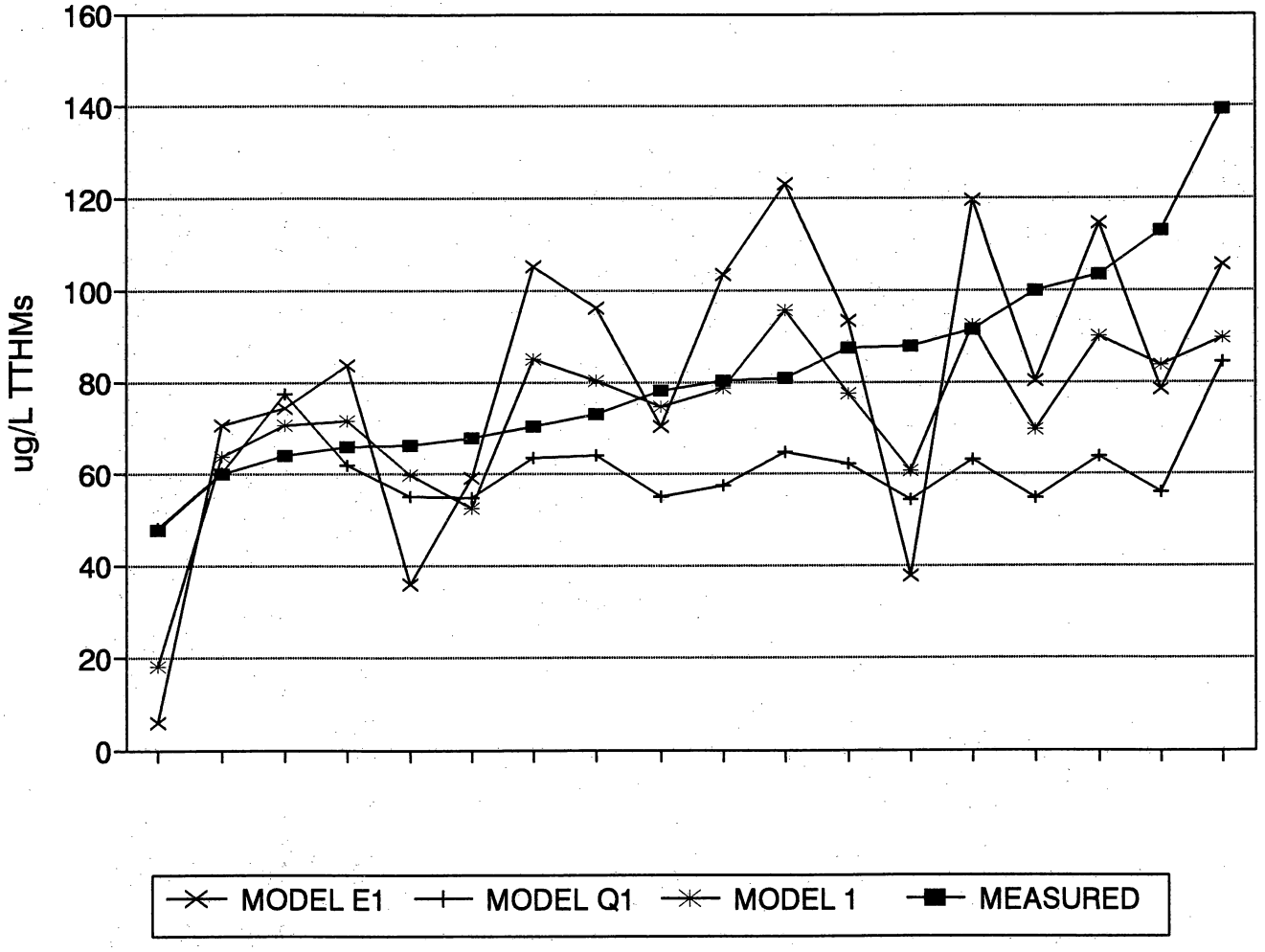
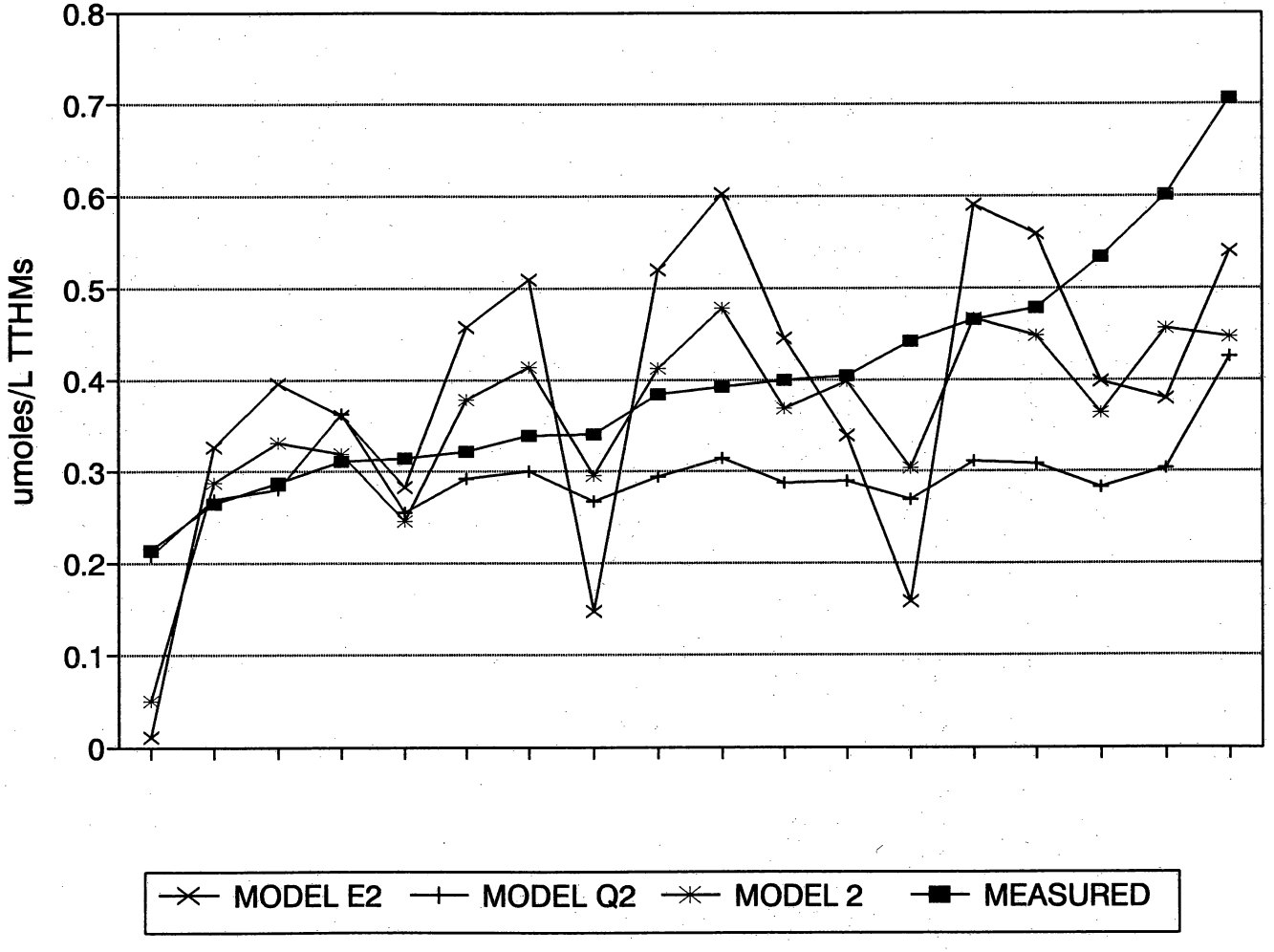


FIGURE 11: 1992 Measured vs Predicted
TTHMs as umoles/L. All new data plotted



the 1992 samples. E1 predicted within ± 20% for only 7 (39%) values in the new data and E2 was even worse with only 5 (28%) predictions within limits. Both E model predicted within 24% for highest TTHM value of 140 which were the closest estimates from any of the models.

The three independent variables found to be significant for the entire database were examined for their individual relationship with ug/L TTHMs. The data in Table 4 shows the correlation coefficients for each independent variable. The slope (B) and constant (C) obtained from the SPSS program can be used to calculate a predicted TTHM value from a known independent variable value using the equation for the best line given previously. Using this method the PIBRMIDE equation predicted ug/L TTHMs within ± 20% for 36% of the 33 measured values in the database. The PICLDOSE equation predicted within ± 20% for 8 of the 9 cases where PICLDOSE was >0. TOTALCL alone predicted within ± 20% of measured TTHMs for 45% of the entire database.

The individual independent variables predicted slightly better for the 1992 data. TOTALCL calculated TTHMs were within ± 20% for 8 of the 18 new samples (44%). PIBRMIDE predicted within ± 20% for 9 of the 18 samples (50%). Two of the new data samples utilized PICLDOSE, but the independent variable equation calculated TTHMs were 22% and 39% off from the measured TTHMs.

DISCUSSION

The first relationship examined was the manner of expression of TTHM concentration. Figure 1 and the correlation coefficients of 0.98 to 1.0 demonstrated that there is no significant difference seen when TTHMs are expressed as *u*g/L, *u*moles/L or *u*g C/L. Several authors have reported similar insignificance when reporting TTHMs as *u*g/L versus *u*moles/L (130,131,132). As TTHMs increased the number of moles and the amount of carbon incorporated increased proportionately in the data examined.

Table 3 and Figures 2 and 3 illustrate each THM's relationship to TTHMs. It is interesting to note that the amount of BDCM and DBCM increase rather consistently with TTHMs. This holds true for mass, molar or carbon concentrations. When CL3 is examined, a mediocre relationship in mass concentration is replaced by a stronger correlation to TTHMs when molar and carbon concentrations are observed. As moles of TTHMs increase the amount of CL3 does also. The difference observed in the mass concentration is no doubt due to the slight atomic weight of CL3 (119.377) compared to the remaining THMs; BDCM (163.828), DBCM (208.280) and BR3 (252.731).

The heaviest weight of BR3 is undoubtedly the reason the slight linear relationship exists between *u*g/L TTHMs and BR3. When moles or incorporated carbon are examined, BR3 does not increase significantly with increasing TTHMs.

The relationships between the individual THM species is interesting as well (Table 3). The higher chlorine containing compounds CL3 and BDCM show a positive correlation (0.795) as does BDCM with DBCM (0.769). The only linear relationship BR3 has is with CL3 and this is an inverse relationship. The fact that when BR3 increases there is a decrease in CL3 has been observed historically on the AVEK data and can be seen on Figures 2 and 3.

The above relationships become factors in the next correlation table produced. Table 4 shows the relationships of the significant independent variables. The fact that the PIBRMIDE correlates strongly with BR3 and only the TTHMs when expressed as mass concentration echoes the relationship of BR3 to TTHMs discussed earlier. The increase in the heavier BR3, due to PIBRMIDE, affects the weight of TTHMs but does not have a strong effect on increasing the number of moles of product. The negative slope of the correlation of PIBRMIDE with CL3 is similar to the negative correlation between CL3 and BR3.

The independent variable PICLDOSE has a positive significant correlation to all the THMs except BR3. Its strongest correlation is with DBCM, the second heaviest THM (Table 4). In Table 3, DBCM had strong linear correlations with all expressions of TTHMs but its strongest was to the mass concentration. The same relationship is seen in the

PICLDOSE with mass concentration of TTHMs having a slightly higher R than the molar or carbon concentrations.

The third important independent variable is TOTALCL. This variable is most strongly correlated to BDCM but also has positive relationships with CL3 and DBCM. Like CL3, BDCM (the second lightest in atomic weight), was more highly correlated with the molar or carbon expressions of TTHMs (Table 3). The same relationship holds true for TOTALCL, a positive correlation with mass concentration gets slightly stronger when moles or carbon incorporation is considered (Table 4).

The independent variables found to be significant ($R > 0.20$, null hypothesis rejected) for the entire database relate to the TTHM concentration in a similar manner as the individual THM with which its highest correlation exists. Slightly different relationships were observed when the database was split into plant samples.

There were only 8 samples from the Rosamond plant. Perhaps the lack of correlations was due to small sample number or the uniqueness of the Rosamond plant. The Rosamond plant is a 14 MGD capacity conventional treatment plant. The plant influent water quality such as PIBRMIDE, PIMPN, PINTU and PIpH can vary from the three other plants in this study due to a 6 million gallon raw water reservoir. This reservoir is in use most of the time and during all sample periods in this study, $KMnO_4$ was applied at the raw

water reservoir inlet at rather low dosages (in all cases <1.2 mg/L). During the day the CWR is filled for a night-time pumping schedule. The lack of correlation with PICLDOSE, which was a significant variable at the other plants, is probably due to only one of the samples had this condition. Chlorination is routinely applied in combination to the TW and PE and specific percentage delivered at each point is unknown. The correlation found between PIBRMIDE and BR3 (R=0.92) is similar to the correlation discussed earlier. The correlation between PINTU and BR3 (R=0.72) may be the indirect effect of the stronger correlation between PINTU and PIBRMIDE (R=0.86) rather than a direct relationship with BR3.

The Eastside (11 samples) and Quartz Hill (13 samples) databases yielded correlations similar to the ones found when the entire database was examined. The PIBRMIDE independent variable again showed a significant relationship to the mass of TTHMs but not to the molar or carbon concentration as displayed in Table 5. The strong correlation between PIBRMIDE and BR3 was observed in both databases as it was in the combined database. The PICLDOSE had the strongest relationship to DBCM in the Q data as in the entire database, but the relationship was stronger to BDCM and CL3 followed by DBCM in the E data. The PICLDOSE shifted slightly also, the stronger correlation was found between PICLDOSE and molar or carbon concentrations of

TTHMs. This may be due to the fact in the E data, PICLDOSE was used only 3 times which corresponded to the 3 highest TOTALCL samples.

TOTALCL behaved similarly to the original data in the E data, having a stronger relationship to the more highly chlorinated species and therefore to the molar or carbon concentrations of TTHMs. This trend was quite apparent in the Q data where no significant correlation was found between TOTALCL and ug/L TTHMs.

Two additional variables, a different one in each database, surfaced with the separation of data (Table 5). PIMPN, which was used as an indication of biological and microbiological activity (based on historical observances) correlated with TTHMs in the E data. However, it did not correlate well with any of the individual THMs. PINTU, also used as an indication of source water quality did correlate with two of the individual THMs in the Q data. Because PINTU had no significant correlation with any form of TTHMs it was not entered into the modeling process.

Determining the variables that most influence the formation of THMs is the first step in making significant reductions in their formation. Model development helps elucidate the relative contributions of each variable. Most researchers agree temperature, pH, precursor source and concentration, reaction time, chlorine dose and bromide concentration all influence the THM equation. This study

uncovered some unusual results in light of "known" relationships. The uniqueness of this study lies in the use of empirical data wherein many variables are varied in different amounts and directions simultaneously. This leads to more complex results than the traditional laboratory jar test or pilot plant experiment where all variables are held constant while only one or two parameters are changed.

Temperature, for instance, has been shown to correlate with the formation of THMs. However, in this data when the temperature was lowest, the bromide concentration was highest. This is a known occurrence in the source water due to the recent drought conditions and pumping schedules in the California Aqueduct (24,25). In fact, for the entire database the correlation coefficient for PIBRMIDE and PITEMP was R=0.39 with a negative slope (inverse relationship).

The lack of influence of pH could be due to the small changes seen in pH in the samples. The range of PIpH for all samples was 7.45 to 8.56 and the CWRpH range was 6.60 to 7.75 (Table 1). The PINTU range was also limited 1.6 to 12 NTU. The lack of significance may be due to lack of range or by the multiple factors in play for these data.

This study does not include a measurement of the precursor concentration and source. The measures taken as an indication of biological activity and general raw water quality were PIMPN and PINTU which would be expected to correlate in a positive direction with TTHMs. Once again,

PIBRMIDE may have masked any possible significant contribution of these variables. PINTU was found to decrease with increasing PIBRMIDE (R=0.42) and PIMPN had a similar relationship. Of course, PINTU and PIMPN are both positively correlated with PITEMP discussed previously, so the overwhelming influence of PIBRMIDE seems evident.

The reaction time is another variable that did not prove as significant as expected. MGD was used as a measure of flow rate which can be considered a measure for the reaction time. This is only a valid measure for each plant considered separately, but even then no significance was observed. The ranges for each plant were: Rm=2.07 to 5.16, E=2.08 to 4.22, and Q=12.4 to 34.7 MGD. No relationships or trends could be seen for MGD, the multiplicity of parameters or lack of range could be the reason.

The chlorine dose did prove to be a significant factor. The point of chlorination when it was at the plant influent, before any precursors had been removed by coagulation and sedimentation, was also significant. The mixed doses, especially those where the dose was split in some undetermined proportion between the PI and TW, may have proven to be significant if the actual chlorine dose at each point could have been entered into the database. This factor may also contribute in a large part to the variability of the predictive models.

The plant influent bromide concentration is shown to be the important factor it has been reported to be. If the actual bromide concentration at the point of chlorination with known doses of chlorine could be separated out, an even more powerful correlation would be expected.

The lack of correlation for $KMnO_4$ use is surprising until the database is examined. It was used at the plant influent at Eastside only 4 times and never at Quartz Hill. The use at Rosamond is misleading because of the application point. $KMnO_4$ may serve to help control biological growth in the raw water reservoir but it has not proved to be a strong enough oxidant to have any effect on TTHMs when used in this manner. A benefit would be to enable the use of lower TOTALCL in the treatment process but this has not been realized.

The significant variables tested for inclusion into models for the prediction of TTHMs were PIBRMIDE, PICLDOSE and TOTALCL for all databases. The E data also included PIMPN. Since all variables had virtually the same statistics for *u*moles/L and *u*g C/L all calculations were performed using *u*g/L or *u*moles/L only.

The final models resulted in six equations, two per database. Scatterplots of residuals and data yielded no indication of any transformations to increase the correlations and predictive ability of the equations. The simple linear mathematical equations were then tested

against the entire database and samples not included in the database. Figures 7, 8 and 9 illustrate the predictive ability of the models. These graphs were developed like the earlier graphs, with the averages of every 3 samples arranged in ascending TTHM order, some variability in the graphs may be attributable to this method.

The examination of each sample in the database and new data proved the Q models to be the best overall predictors of TTHMs. Models 1 & 2 predicted next best in the database, and better in the new data tested. E1 and E2 proved to be not suitable for use as for accurate predictions in most cases.

The model was determined to predict well if it came within $\pm$ 20% of the measured value. The independent variables were measured in the same way. TOTALCL was found to predict TTHMs in 45% and PIBRMIDE in 41% of all samples (33 in database and 18 new). PICLDOSE alone predicted very well when PICLDOSE was in use (only 11 cases total, 9 in database).

CONCLUSIONS

The best overall models turned out to be the two developed on the Quartz Hill (Q) database (Q1 and Q2). These models predicted within ± 20% of the measured TTHMs for 70% (Q2) and 67% (Q1) of the samples in the database. Of the new samples not used in the database, 44% of the values were predicted within ± 20% by Q1 and Q2:

Model Q1: ug/L TTHMs = 30.3423 + 1.1938(TOTALCL) + 60.3345(PIBRMIDE) + 11.2827(PICLDOSE)

Model Q2: umoles/L TTHMs = 0.1416 + 0.02885 (TOTALCL) + 0.1335(PIBRMIDE) + 0.06126(PICLDOSE)

The Model 1 proved to be the best predictor for the new data values (61%) with Model 2 within ± 20% for 56% of the new data values.

Model 1: ug/L TTHMs = -32.8234 + 19.3378 (TOTALCL) + 114.6749(PIBRMIDE) + 2.9133(PICLDOSE)

Model 2: umoles/L TTHMs = -0.1871 + 0.1268 (TOTALCL) + 0.3962(PIBRMIDE) + 0.01325(PICLDOSE)

The variability in the entire database may have come from including the Rosamond (Rm) data. When separated the Rm data did not exhibit the same correlations within as did the Q and Eastside (E) data.

The model development helped elucidate the relative contributions of each of the independent variables tested. The relationships between the independent variables and the individual THMs is the basis for the relationships found between the independent variables and TTHMs. This knowledge helps clarify how the independent variables influence final TTHM concentrations.

The total chlorine dose in mg/L (TOTALCL) proved to be the most significant influence on TTHMs of those studied. An increase in TOTALCL results in increasing the mass concentration of TTHMs. However, TOTALCL has an even stronger positive correlation with total moles of TTHMs and amount of carbon incorporated into TTHMs. How this occurs can be seen in the positive relationships between TOTALCL and chloroform (CL3), bromodichloromethane (BDCM) and dibromochloromethane (DBCM). This lies in the fact that with more available chlorine to form substitutions into the organohalides, the more chlorinated by-products are formed. The lighter weight of the incorporated chlorine (as opposed to bromine) does not have as much impact on the total mass as it does on the total number of moles formed.

The significance of chlorine is strengthened when point of application is at the plant influent (PICLDOSE). If chlorine is applied at the plant influent, before any treatment has removed precursor material, the TTHMs are increased. The higher the dose, the more TTHMs are formed, no matter how they are expressed. In the separated data, the relationship between increasing PICLDOSE and moles of TTHMs or incorporated carbon is stronger than for mass, as seen above for TOTALCL. When the entire database is observed, a strong correlation was found between the second heaviest THM, DBCM, and PICLDOSE such that the influence was about equal on all forms of TTHM expression.

The bromide concentration (PIBRMIDE) was found to be a significant contributor to ug/L TTHMs. This is accomplished by increasing the amount of bromoform (BR3), the heaviest of the TTHMs. An additional relationship was also seen in the Q data where PIBRMIDE increased the amount of the second heaviest THM, DBCM. These relationships are similar to chlorine as discussed earlier. The more bromine available for incorporation into organohalides, the more brominated THMs will be formed. In fact, the kinetics of the reaction as discussed earlier have been shown to produce the brominated species quicker and preferentially when bromide is present.

PIBRMIDE did not prove to be valuable for use as a surrogate for TTHMs. The correlation with BR3 and DBCM is

significant, and it does show a positive relationship with increasing ug/L TTHMs, but this alone is not enough for PIBRMIDE to accurately predict TTHMs.

The fact that PIBRMIDE does not have a significant relationship with moles of THMs or amount of carbon incorporated into TTHMs is interesting. Bromide is thought to be incorporated preferentially into the THMs. The negative relationship between CL3 and BR3 seems to confirm this. While no more moles of product are formed or carbon incorporated in TTHMs, the mass is increased with increased PIBRMIDE. Bromoform is formed at the expense of chloroform when bromide is present.

The purpose of this study was to develop a predictive model for conventional treatment of the California Aqueduct source water. Most predictive modeling efforts have been found to be source specific. This model may not be as accurate as desired for other sources because there is no variable representing precursor materials or concentrations.

The predictive ability of the best model was found to be valid for 61% of the new samples not included in the database. This model will prove useful as a baseline to judge what the expected TTHMs should be and help in the evaluation of changes in source water quality or varying treatment parameters.

APPENDIX A: ABBREVIATIONS

A: Acton Water Treatment Plant

ALUM: Aluminum sulfate

AWWA: American Water Works Association

AVEK: Antelope Valley East Kern Water Agency

BDCM: Bromodichloromethane

BR3: Bromoform (Tribromomethane)

CARBON: Powdered Activated Carbon

CL3: Chloroform (Trichloromethane)

ClO_2: Chlorine Dioxide

CWR: Clear Well Reservoir (finished water)

CWRpH: Clear Well Reservior pH

DBCM: Dibromochloromethane

DBPs: Disinfection By-products

E: Eastside Water Treatment Plant

ECP: Extracellular products

EPA: United States Environmental Protection Agency

$KMnO_4$: Potassium permanganate

MCL: Maximum Contaminant Level

MGD: Million gallons per day

mg/L: milligrams per liter

***ug*/L:** micrograms per liter

***ug* C/L:** micrograms Carbon per liter

***umoles*/L:** micromoles per liter

MPN: Most Probable Number per 100 milliliters, an estimate of bacterial density.

NORS: National Organics Reconnaissance Survey

NTU: Nephlometric Turbidity Units

PI: Plant Influent

PIBRMIDE: Plant Influent Bromide Concentration in mg/L

PIMPN: Plant Influent Bacterial Density in MPN

PINTU: Plant Influent Turbidity in NTU

PIpH: Plant Influent pH

PITEMP: Plant Influent Temperature in °C

POLY: Cationic polymer

Q: Quartz Hill Water Treatment Plant

RESIDCL2: Total residual chlorine in the CWR

Rm: Rosamond Water Treatment Plant

SDWA: Safe Drinking Water Act

THMs: Trihalomethanes (BR3, CL3, BDCM and DBCM)

TTHMs: Total Trihalomethanes; the sum of all four compounds

TOC: Total Organic Carbon

TOTALCL: Total chlorine dose applied during treatment

UV: Ultraviolet light

FOOTNOTES

1. Abelson, P.H. 1990. "Volatile Contaminants in Drinking Water." Science 247(4939):141.

2. Watts, T.E. & Singer, R.D. 1990. "Drinking Water Contaminants: Sources, Health Considerations, and Removal." Minn. Medicine 73:33.

3. USA Today. 1989. "Toxicology: Can Chlorine Cause Cancer?" USA Today 117(2525):14.

4. Olson, B.H. 1989. "The Safety of Our Drinking Water." New England J. of Med. 320(21):1413.

5. Lykins, B.W. Jr.; Koffskey, W.E. & Miller, R.G. 1986. "Chemical Products and Toxicologic Effects of Disinfection." JAWWA 78(11):66.

6. Bull, R.J. 1979. "Health Effects of Alternate Disinfectants and Their Reaction Products." Proceedings AWWA annual conference.

7. Calabrese, E.J.; Gilbert, C.E. & Pastides, H. eds. 1989. "Safe Drinking Water Act: Amendments, Regulations and Standards." Lewis Pub. Inc., Chelsea, Mich.

8. McGuire, M.J. 1989. "Preparing for the Disinfection By-Product Rule: A Water Industry Status Report." JAWWA 81(8):35.

9. Cotruvo, J.A. & Wu, C. 1978. "Controlling Organics: Why Now?" JAWWA 70(11):590.

10. Federal Register. 1975. Vol.40(248):Chapter 1, part 141.

11. Symons, J.M.; Bellar, T.A.; Carswell, J.K.; DeMarco, J.; Kropp, K.L.; Robeck, G.G.; Seeger, D.R.; Slocum, C.J.; Smith, B.L. & Stevens, A.A. 1975. "National Organics Reconnaissance Survey for Halogenated Organics." JAWWA 67(11):634.

12. Bellar, T.A.; Lichtenberg, J.J. & Kroner, R.C. 1974. "The Occurrence of Organohalides in Chlorinated Drinking Waters." JAWWA 66(12):703.

13. Moser, R.H. & Lee, R.G. 1983. "Field Experiences with Controlling TTHMs." Proceedings of AWWA Seminar on Strategies for the Control of Trihalomethanes.

14. Rook, J.J. 1974. "Formation of Haloforms During Chlorination of Natural Waters." J. Water Trtmt. Exam. 23:234.

15. Trussell, R.R. & Umphres, M.D. 1978. "The Formation of Trihalomethanes." JAWWA 70(11)604.

16. Federal Register. 1979. Vol.40(248): Chapter 1, part 141.

17. Federal Register. 1986. Vol.40(248): Chapter 1, part 141.

18. Smith, G.J. 1990. Participant in a roundtable discussion: "Additives" JAWWA 82(10):28.

19. ACWA Seminar "1990 Workshop on Drinking Water Regulations" Sponsored by Association of California Water Agencies in consultation with PRECOR Corp. & Regulatory Network, Inc. 1990.

20. Krasner, S.W.; Sclimenti, M.J.; Means, E.G.; Symons, J.M. & Simms, L. 1992. "The Impact of Chlorine Dose, Residual Chlorine, Bromide and Organic Carbon on Trihalomethane Speciation. Presented at the AWWA WQTC, Toronto, Canada.

21. M.A.S. 1990. "Theme Introduction: Toxicology." JAWWA 82(10):43.

22. McGuire, M.J. & Meadow, R.G. 1988. "AWWARF Trihalomethane Survey." JAWWA 80(1):61.

23. J.H. "Theme Introduction: Organics." 1990. JAWWA 82(1):37.

24. Delta Islands Drainage Investigation. 1990. "Report: A Summary of Observations During Consecutive Dry Year Conditions, Water years 1987 and 1988." draft received from Bruce Agee, State of California, Department of Water Resources.

25. Interagency Delta Health Aspects Monitoring Program. 1989. "The Delta as a Source of Drinking Water." Department of Water Resources, State of California.

26. MWD. 1990. "Gambling with a Water Supply." Focus 5. (A publication of the Metropolitan Water District of Southern California).

27. Brown & Caldwell, consulting engineers. 1989. "Delta Drinking Water Quality Study." performed for the California Urban Water Agencies.

28. Krasner, S.W. 1990. "Evaluation of THM Precursor Contributions from Agricultural Drains." JAWWA 82(1):57.

29. State Water Resources Control Board. 1991. "Delta Water Quality: A Report to the Legislature on Trihalomethanes and the Quality of Drinking Water Available from the Sacramento-San Joaquin Delta." State of California, Department of Health Services.

30. Greenberg, A.E. 1980. "Chlorination of Drinking Water - Public Health Perspectives." in Water Chlorination: Environmental Impact and Health Effects. Jolley, R.L.; Brungs, W.A.; & Cumming, R.B., eds. Ann Arbor Sci. Pub.,Inc., Ann Arbor, Mich.

31. AWWA. 1973. Water Chlorination Principles and Practices. AWWA Manual M20. AWWA, Denver, CO.

32. Neal, R.A. 1990. "Assessing Toxicity of Drinking Water Contaminants." JAWWA 82(10):44.

33. Meier, J.R. & Daniel, F.B. 1990. "The Role of Short-Term Tests in Evaluating Health Effects Associated with Drinking Water." JAWWA 82(10):48.

34. Bull, R.J. 1990. "Cancer Risk Assessment: Importance of Identifying Mechanisms of Action." JAWWA 82(10):57.

35. Daniel, F.B.; Condie, L.W.; Robinson, M.; Stober, J.A.; York, R.G.; Olson, G.R. & Wang, S.-R. 1990. "Comparative Subchronic Toxicity Studies of Three Disinfectants." JAWWA 82(10):61.

36. M.F.G. 1978. "Theme Introduction: Controlling Organics." JAWWA 70(11):589.

37. I.M.S. 1984. "Theme Introduction: Combating Organic Contaminants." JAWWA 76(4):121.

38. I.M.S. 1982. "Theme Introduction: Controlling Organics - Research Update." JAWWA 74(2):57.

39. Rook, J.J. 1976. "Haloforms in Drinking Water." JAWWA 68(3)168.

40. Morris, J.C. 1986. "Aqueous Chlorine in the Treatment of Water Supplies." in Organic Carcinogens in Drinking Water. Ram, N.M.; Calabrese, E.J. & Christman, R.F. eds. John Wiley & Sons, N.Y.

41. Johnson, J.D. & Jensen, J. 1983. "THM and TOX Formation - Routes, Rates and Precursors." Proceedings of AWWA seminar on Strategies for the Control of Trihalomethanes.

42. Rebhun, M.; Manka, J. & Zilberman, A. 1988. "Trihalomethane Formation in High-Bromide Lake Galilee Water." JAWWA 80(6):84.

43. Cooper, W.J.; Zika, R.G. & Steinhauer, M.S. 1985. "Bromide-Oxidant Interactions and THM Formation: A Literature Review." JAWWA 77(4):116.

44. Dore, M.; Merlet, N.; DeLaat, J. & Goichan, J. 1982. "Reactivity of Halogens with Aqueous Micropollutants: A Mechanism for the Formation of Trihalomethanes." JAWWA 74(2):103.

45. Kalbus, L.H. 1993. personal communication.

46. Jolles, Z.E. ed. 1966. Bromine and Its Compounds. Ernest Benn Ltd.,London.

47. Lange, A.L. & Kawczynski, E. 1978. "Controlling Organics: The Contra Costa County Water District Experience." JAWWA 70(11):653.

48. Kavanaugh, M.C.; Trussell, A.R.; Cromer, J. & Trussell, R.R. 1980. "An Empirical Kinetic Model of Trihalomethane Formation: Applications to Meet the Proposed THM Standard." JAWWA 72(10):578.

49. Symons, J.M.; Stevens, A.A.; Clark, R.M.; Geldreich, E.E.; Love, O.T. Jr. & DeMarco, J. 1981. "Removing Trihalomethanes from Drinking Water." Water Eng. & Mngmt. July, p.50.

50. Bunn, W.W.; Haas, B.B.; Deane, E.R. & Kleopfer, R.D. 1975. "Formation of Trihalomethanes by Chlorination of Surface Water." Environ. Letters 10(3):205.

51. Brass, H.J. 1982. "Procedures for Analyzing Organic Contaminants in Drinking Water." JAWWA 74(2):107.

52. Morrow, C.M. & Minear, R.A. 1984. "Determination of Bromide in Natural Waters by Ion Chromatography using a Concentrator Column." Water Res. 18(9);1165.

53. Amy, G.L.; Minear, R.A. & Cooper, W.J. 1987. "Testing and Validation of a Multiple Nonlinear Regression Model for Predicting Trihalomethane Formation Potential." Water Res. 21(6):649.

54. Amy, G.L.; Chadik, P.A. & Chowdhury, Z.K. 1987. "Developing Models for Predicting Trihalomethane Formation Potential and Kinetics." JAWWA 79(7):89.

55. Cameron, G.N.; Symons, J.M.; Spencer, S.R. & Ma, J.Y. 1989. "Minimizing THM Formation During Control of the Asiatic Clam: A Comparison of Biocides." JAWWA 81(8):61.

56. Symons, J.M.; Fu, P.L.K.; Dressman, R.C. & Stevens, A.A. 1987. "The Influence of Bromide Ion on Organic Chlorine and Organic Bromine Formation During Free Chlorination." JAWWA 79(9):114.

57. Krasner, S.W.; McGuire, M.J.; Jacangel, J.G.; Patania, N.L.; Reagan, K.M. & Aieta, E.M. 1989. "The Occurrence of Disinfection By-Products in US Drinking Water." JAWWA 81(8):41.

58. Stevens, A.A.; Slocum, C.J.; Seeger, D.R. & Robeck, G.G. 1976. "Chlorination of Organics in Drinking Water." JAWWA 68(11):615.

59. Johnson, J.D. & Jensen, J.N. 1986. "THM and TOX Formation: Routes, Rates and Precursors." JAWWA 78(4):156.

60. Singer, P.C. & Chang, S.D. 1989. "Correlations Between Trihalomethanes and Total Organic Halides Formed During Water Treatment." JAWWA 81(8):61.

61. Urano, K.; Wada, H. & Takemasa, T. 1983. "Empirical Rate Equation for Trihalomethane Formation with Chlorination of Humic Substances in Water." Water Res. 17(12):1797.

62. Virchem Co. "Reduction of Trihalomethanes in Potable Water Systems." Technical Data by Virchem.

63. Singer, P.C.; Barry, J.J.III; Palen, G.M. & Scrivner, A.E. 1981. "Trihalomethane Formation in North Carolina Drinking Waters." JAWWA 73(8):392.

64. Knocke, W.R.; West, S. & Hoehn, R.C. 1986. "Effects of Low Temperature on the removal of Trihalomethane Precursors by Coagulation." JAWWA 78(4):189.

65. AWWA Research Foundation. 1978. "Organics Removal Project." Synopsis by AWWA Res. Found., Denver, CO.

66. Huck, P.M. 1990. "Measurement of Biodegradable Organic Matter and Biological Growth Potential in Drinking Waters." JAWWA 82(7):78.

67. Joyce, W.S.; DiGiano, F.A. & Uden, P.C. 1984. "THM Precursors in the Environment." JAWWA 76(6):102.

68. Collins, M.R.; Amy, G.L. & Steelink, C. 1986. "Molecular Weight Distribution, Carboxylic Acidity, and Humic Substances Content of Aquatic Organic Matter: Implications for Removal during Water Treatment." Environ. Sci. Technol. 20:1028-1032.

69. Reckhow, D.A. & Singer, P.C. 1990. "Chlorination By-Products in Drinking Waters: From Formation Potentials to Finished Water Concentrations." JAWWA 82(4):173.

70. Chadik, P.A. & Amy, G.L. 1987. "Coagulation and Adsorption of Humic Substances: An Analysis of Surrogate Parameters for Predicting Effects on Trihalomethane Formation Potential." Environ. Tech. Letters. 8:261.

71. Zelibor, J.L.Jr.; Romankiw, L.; Hatcher, P.G. & Colwell, R.R. 1988. "Comparative Analysis of the Chemical Composition of Mixed and Pure Cultures of Green Algae and Their Decomposition Residues by ^{13}C Nuclear Magnetic Resonance Spectroscopy." Appl. & Environ. Microbiol. 54(4):1051.

72. Hoehn, R.C.; Barnes, D.B.; Thompson, B.C.; Randall, C.W.; Grizzard, T.J. & Shaffer, P.T.B. 1980. "Algae as Sources of Trihalomethane Precursors." JAWWA 72(6):344.

73. Briley, K.F.; Williams, R.F.; Longley, K.E. & Sorber, C.A. 1980. "Trihalomethane Production from Algal Precursors." in Water Chlorination: Environmental Impact and Health Effects. Vol. 3. Jolley, R.L.; Brungs, W.A.; Cumming, R.B. & Jacobs, V.A. eds. Ann Arbor Science, Ann Arbor, Mich.

74. Scully, F.E., Jr.; Howell, G.D.; Jewell, J.T. 1980. "Proteins in Natural Waters and Their Relations to the Formation of Chlorinated Organics During Water Treatment." Environ. Sci. Technol. 22(5):537.

75. Semmens, M.J. & Ayers, K. 1985. "Removal by Coagulation of Trace Organics from Mississippi River Water." JAWWA 77(5):79.

76. Feige, M.A.; Glick, E.M.; Munch, J.W.; Munch, D.J.; Noschang, R.L. & Brass, H.J. 1980. "Potential Contaminants Introduced into Water Supplies by Use of Coagulant Aids." in Water Chlorination: Environmental Impact and Health Effects. Vol. 3. Jolley, R.L.; Brungs, W.A. & Cumming, R.B., eds. Ann Arbor Sci., Ann Arbor, Mich.

77. Glaser, H.T. & Edzwald, J.K. 1979. "Coagulation and Direct Filtration of Humic Substances with Polyethylenamine." Environ. Sci. Technol. 13(3):299.

78. AWWA Coagulation Committee. 1989. "Committee Report: Coagulation as an Integrated Water Treatment Process." JAWWA 81(10):72.

79. Randtke, S.J. 1988. "Organic Contaminant Removal by Coagulation and Related Process Combinations." JAWWA 80(5):40.

80. Dentel. S.K. & Gossett, J.M. 1988. "Mechanisms of Coagulation with Aluminum Salts." JAWWA 80(4):187.

81. Bales, R.C. 1986. "Surface Chemistry in Water Treatment: Reactions at the Solid-Liquid Interface." JAWWA 78(11):59.

82. Hundt, T.R. & O'Melia, C.R. 1988. "Aluminum-Fulvic Acid Interactions: Mechanisms and Applications." JAWWA 80(4):176.

83. Singh, I.M. & McTighe, T.C. 1982. "Reducing the Formation of Trihalomethanes." Public Works 113(8):45.

84. Davenport, R.J.; Wynveen, R.A. & Cooper, W.J. 1981. "Continuous, Automated, and Low-Cost Monitoring of the Organic Content in Water." JAWWA 73(10):555.

85. Prescott, G. 1964. How to Know the Fresh Water Algae. W.M.C. Brown, Co. Pub., Dubuque, Iowa.

86. Lewin, R.A. 1962. Physiology and Biochemistry of Algae. Academic Press, NY.

87. Stewart, W.B.P., ed. 1974. Algal Physiology and Biochemistry. U. California Press, Los Angeles.

88. Harrington, D. 1993. personal communication.

89. Amy, G.L.; Collins, M.R.; Kuo, C.J. & King, P.H. 1987. "Comparing Gel Permeation Chromatography and Ultrafiltration for the Molecular Weight Characterization of Aquatic Organic Matter." JAWWA 79(1):43.

90. Levine, A.D.; Baumann, E.R. & Lind, L.B. 1987. "Curbing THMs in Small Water Systems." JAWWA 79(5):52.

91. Jodellah, A.M. & Weber, W.J., Jr. 1985. "Controlling Trihalomethane Formation Potential by Chemical Treatment and Adsorption." JAWWA 77(10):95.

92. Singer, P.C. 1983. "Applicability of Coagulants and Alternative Oxidants for Controlling THM Formation." Proceedings of AWWA Seminar on Strategies for the Control of Trihalomethanes. AWWA, Denver, CO.

93. Dempsey, B.A.; Ganho, R.M. & O'Melia, C.R. 1984. "The Coagulation of Humic Substances by Means of Aluminum Salts." JAWWA 76(4):141.

94. Weber, W.J., Jr. & Jodellah, A.M. 1985. "Removing Humic Substances by Chemical Treatment and Adsorption." JAWWA 77(4):132.

95. Hoehn, R.C.; Dixon, K.L.; Malone, J.K.; Novak, J.T. & Randall, C.W. 1984. "Biologically Induced Variations in the Nature and Removability of THM Precursors by Alum Treatment." JAWWA 76(4):134.

96. Kavanaugh, M.C. 1978. "Modified Coagulation for Improved Removal of Trihalomethane Precursors." JAWWA 70(11):613.

97. Semmens, M.J.; Norgaard, G.E.; Hohenstein, G. & Staples, A.B. 1986. "Influence of pH on the Removal of Organics by Granular Activated Carbon." JAWWA 78(5):89.

98. Hubel, R.E. & Edzwald, J.K. 1987. "Removing Trihalomethane Precursors by Coagulation." JAWWA 79(7):98.

99. Colthurst, J.M. & Singer, P.C. 1987. "Removing Trihalomethane Precursors by Coagulation." JAWWA 79(7):98.

100. Carns, K.E. & Stinson, K.B. 1978. "Controlling Organics: The East Bay Municipal Utility District Experience." JAWWA 70(11):637.

101. Stevens, A.A.; Moore, L.A. & Miltner, R.J. 1989. "Formation and Control of Non-Trihalomethane Disinfection By-Products." JAWWA 81(9):54.

102. McBride, D.G. 1978. "Controlling Organics: The Los Angeles Department of Water and Power Experience." JAWWA 70(11):644.

103. Myers, A.G. 1990. "Evaluating Alternative Disinfectants for THM Control in Small Systems." JAWWA 82(6):77.

104. Reckhow, D.A. & Singer, P.C. 1984. "The Removal of Organic Halide Precursors by Preozonation and Alum Coagulation." JAWWA 76(4):151.

105. APHA, AWWA, & WPCF. Franson, M.A., managing ed. 1976. Standard Methods for the Examination of Water and Wastewater. 14th ed. American Public Health Assoc., Washington, D.C.

106. Sorber, C.A.; Williams, R.F.; Moore, B.E. & Longley, K.E. 1982. "Alternative Water Disinfection Schemes for Reduced Trihalomethane Formation: Vol. 1. Prototype Studies." USEPA Project Summary. EPA pub. no. 600/S2-82-037.

107. Smith, G.G. 1991. personal communication.

108. Singer, P.C.; Borchardt, J.H. & Colthurst, J.M. 1980. "The Effects of Permanganate Pretreatment on Trihalomethane Formation in Drinking Water." JAWWA 72(10):573.

109. Werdehoff, K.S. & Singer, P.C. 1987. "Chlorine Dioxide Effects on THMFP, TOXFP, and the Formation of Inorganic By-Products." JAWWA 79(9):107.

110. Fecek, K.J. & Boll, J.E. 1981. "Potassium Permanganate: An Alternative to Prechlorination." Carus Chem. Corp., La Salle, Ill.

111. Aieta, E.M. & Berg, J.D. 1986. "A Review of Chlorine Dioxide in Drinking Water Treatment." JAWWA 78(6)62.

112. Lykins, B.W., Jr. & Griese, M.H. 1986. "Using Chlorine Dioxide for Trihalomethane Control." JAWWA 78(6):62.

113. Argaman, Y.; Shelley, S.E., Jr.; Davis, J.S.; Betts, S.C. & Hufft, R.J., Jr. 1984. "Preventing Haloform Formation in Treated Surface Water: A Case Study." JAWWA 76(4):172.

114. Pfaff, J.D. & Brockhoff, C.A. 1990. "Determining Inorganic Disinfection By-Products by Ion Chromatography." JAWWA 82(4):192.

115. Thompson, J.C. & Amens, J.J. 1987. "Preventing the Formation of Trihalomethanes in Florida Groundwater." JAWWA 79(1):38.

116. LaFrance, P. & Mozet, M. 1989. "Adsorption of Humic Substances in the Presence of Sodium Salts." JAWWA 81(4):155.

117. Lykins, B.W., Jr.; Clark, R.M. & Adams, J.Q. 1988. "Granular Activated Carbon for Controlling THMs." JAWWA 80(5):85.

118. Glaze, W.H. & Wallace, J.L. 1984. "Control of Trihalomethane Precursors in Drinking Water: Granular Activated Carbon With and Without Preozonation." JAWWA 76(2):68.

119. Roberts, P.V. & Summers, R.S. 1982. "Performance of Granular Activated Carbon for Total Organic Carbon Removal." JAWWA 74(2):113.

120. Liao, M.Y. & Randtke, S.J. 1985. "Removing Fulvic Acid by Lime Softening." JAWWA 77(8):78.

121. Edwards, E.D.; Watson, I. & McKenna, D.C. 1990. "THM Control Using Membrane Technology - Fort Myers Case Study." Boyle Engineering Report. (consultants for AVEK Water Agency, Quartz Hill, CA).

122. Fu, P.L.K. & Symons, J.M. 1990. "Removing Aquatic Organic Substances by Anion Exchange Resins." JAWWA 82(10):70.

123. O'Kouchi, S. & Saegusa, H. 1989. "Determination of Volatilization Coefficients of Trihalomethanes from Waters." Water Sci. Technol. 21(12):1907.

124. Croue, J-P. & Reckhow, D.A. 1989. "Destruction of Chlorination By-Products with Sulfite." Environ. Sci. Technol. 23(11):1412.

125. Brown and Caldwell. 1990. "Sanitary Survey of the State Water Project: Final Report." Brown and Caldwell, consultants for the California State Water Contractors.

126. Smith, Maureen M. 1988. Treatment Practices to Lower THMs: A Three Year Study. Presentation to the Antelope Valley East Kern Water Agency Board of Directors.

127. Crittenden, J.C. & Hand, D.W. 1983. "Design Considerations for GAC Treatment of Synthetic Organic Chemicals and TOC." Proceedings of AWWA Seminar on Strategies for the Control of Trihalomethanes. AWWA, Denver, CO.

128. Batchelor, B.; Fusilier, D. & Murray, E.H. 1987. "Developing Haloform Formation Potential Tests." JAWWA 79(1):50.

129. Edzwald, J.K.; Becker, W.C. & Wattier, K.L. 1985. "Surrogate Parameters for Monitoring Organic Matter and THM Precursors." JAWWA 77(4):122.

130. Edzwald, J.K. 1986. "Conventional Water Treatment and Direct Filtration: Treatment and Removal of Total Organic Carbon and Trihalomethane precursors." in Organic Carcinogens in Drinking Water. Ram, N.M.; Calabrese, E.J. & Christman, R.J., eds. John Wiley and Sons. NY.

131. Heath, J.; Agee, B. & Jung, M. 1989. The Delta as a Source of Drinking Water: Monitoring Results 1983 to 1987. Interagency Delta Health Aspects Monitoring Program. Dept. of Water Resources, State of California.

132. Chowdhury, Z.K. 1984. Development and Comparison of Linear and Nonlinear Multiple Regression Models for Predicting Trihalomethane Formation Kinetics. U. Arizona. Master's Thesis.

133. Fraas, T.B. 1984. Multiple Linear Regression Models for Predicting Trihalomethane Formation from Chlorinated Natural Waters. U. Arizona. Master's Thesis.

134. Chadik, P.A. 1985. Modeling Trihalomethane Formation in Drinking Water After Alum Coagulation or Activated Carbon Adsorption. U. Arizona, Doctoral Dissertation.

BIBLIOGRAPHY*

Abelson, P.H. 1990. "Volatile Contaminants in Drinking Water." Science 247(4939):141. (1)

ACWA Seminar "1990 Workshop on Drinking Water Regulations" Sponsored by Association of California Water Agencies in consultation with PRECOR Corp. & Regulatory Network, Inc. 1990. (19)

Aieta, E.M. & Berg, J.D. 1986. "A Review of Chlorine Dioxide in Drinking Water Treatment." JAWWA 78(6)62. (111)

Amy, G.L.; Collins, M.R.; Kuo, C.J. & King, P.H. 1987. "Comparing Gel Permeation Chromatography and Ultrafiltration for the Molecular Weight Characterization of Aquatic Organic Matter." JAWWA 79(1):43. (89)

Amy, G.L.; Minear, R.A. & Cooper, W.J. 1987. "Testing and Validation of a Multiple Nonlinear Regression Model for Predicting Trihalomethane Formation Potential." Water Res. 21(6):649. (53)

Amy, G.L.; Chadik, P.A. & Chowdhury, Z.K. 1987. "Developing Models for Predicting Trihalomethane Formation Potential and Kinetics." JAWWA 79(7):89. (54)

APHA, AWWA, & WPCF. Franson, M.A., managing ed. 1976. Standard Methods for the Examination of Water and Wastewater. 14th ed. American Public Health Assoc., Washington, D.C. (105)

Ibid. 1989. 17th ed.

Ibid. 1992. 18th ed.

Argaman, Y.; Shelley, S.E., Jr.; Davis, J.S.; Betts, S.C. & Hufft, R.J., Jr. 1984. "Preventing Haloform Formation in Treated Surface Water: A Case Study." JAWWA 76(4):172. (113)

AWWA. 1973. Water Chlorination Principles and Practices. AWWA Manual M20. AWWA, Denver, CO. (31)

AWWA Coagulation Committee. 1989. "Committee Report: Coagulation as an Integrated Water Treatment Process." JAWWA 81(10):72. (78)

AWWA Research Foundation. 1978. "Organics Removal Project." Synopsis by AWWA Res. Found., Denver, CO. (65)

Bales, R.C. 1986. "Surface Chemistry in Water Treatment: Reactions at the Solid-Liquid Interface." JAWWA 78(11):59. (81)

Batchelor, B.; Fusilier, D. & Murray, E.H. 1987. "Developing Haloform Formation Potential Tests." JAWWA 79(1):50. (128)

Bellar, T.A.; Lichtenberg, J.J. & Kroner, R.C. 1974. "The Occurrence of Organohalides in Chlorinated Drinking Waters." JAWWA 66(12):703. (12)

Brass, H.J. 1982. "Procedures for Analyzing Organic Contaminants in Drinking Water." JAWWA 74(2):107. (51)

Briley, K.F.; Williams, R.F.; Longley, K.E. & Sorber, C.A. 1980. "Trihalomethane Production from Algal Precursors." in Water Chlorination: Environmental Impact and Health Effects. Vol. 3. Jolley, R.L.; Brungs, W.A.; Cumming, R.B. & Jacobs, V.A. eds. Ann Arbor Science, Ann Arbor, Mich. (73)

Brown & Caldwell, consulting engineers. 1989. "Delta Drinking Water Quality Study." performed for the California Urban Water Agencies. (27)

Brown and Caldwell. 1990. "Sanitary Survey of the State Water Project: Final Report." Brown and Caldwell, consultants for the California State Water Contractors. (125)

Bull, R.J. 1979. "Health Effects of Alternate Disinfectants and Their Reaction Products." Proceedings AWWA annual conference. (6)

Bull, R.J. 1990. "Cancer Risk Assessment: Importance of Identifying Mechanisms of Action." JAWWA 82(10):57. (34)

Bunn, W.W.; Haas, B.B.; Deane, E.R. & Kleopfer, R.D. 1975. "Formation of Trihalomethanes by Chlorination of Surface Water." Environ. Letters 10(3):205. (50)

Calabrese, E.J.; Gilbert, C.E. & Pastides, H. eds. 1989. "Safe Drinking Water Act: Amendments, Regulations and Standards." Lewis Pub. Inc., Chelsea, Mich. (7)

Cameron, G.N.; Symons, J.M.; Spencer, S.R. & Ma, J.Y. 1989. "Minimizing THM Formation During Control of the Asiatic Clam: A Comparison of Biocides." JAWWA 81(8):61. (55)

Carns, K.E. & Stinson, K.B. 1978. "Controlling Organics: The East Bay Municipal Utility District Experience." JAWWA 70(11):637. (100)

Chadik, P.A. 1985. Modeling Trihalomethane Formation in Drinking Water After Alum Coagulation or Activated Carbon Adsorption. U. Arizona, Doctoral Dissertation. (134)

Chadik, P.A. & Amy, G.L. 1987. "Coagulation and Adsorption of Humic Substances: An Analysis of Surrogate Parameters for Predicting Effects on Trihalomethane Formation Potential." Environ. Tech. Letters. 8:261. (70)

Chowdhury, Z.K. 1984. Development and Comparison of Linear and Nonlinear Multiple Regression Models for Predicting Trihalomethane Formation Kinetics. U. Arizona. Master's Thesis. (132)

Cohen, R.S.; Hwang, C.J. & Krasner, S.W. 1978. "Controlling Organics: The Metropolitan Water District of Southern California Experience." JAWWA 70(11):647.

Collins, M.R.; Amy, G.L. & Steelink, C. 1986. "Molecular Weight Distribution, Carboxylic Acidity, and Humic Substances Content of Aquatic Organic Matter: Implications for Removal during Water Treatment." Environ. Sci. Technol. 20:1028-1032. (68)

Cooper, W.J.; Zika, R.G. & Steinhauer, M.S. 1985. "Bromide-Oxidant Interactions and THM Formation: A Literature Review." JAWWA 77(4):116. (43)

Colthurst, J.M. & Singer, P.C. 1987. "Removing Trihalomethane Precursors by Coagulation." JAWWA 79(7):98. (99)

Cotruvo, J.A. & Wu, C. 1978. "Controlling Organics: Why Now?" JAWWA 70(11):590. (9)

Crittenden, J.C. & Hand, D.W. 1983. "Design Considerations for GAC Treatment of Synthetic Organic Chemicals and TOC." Proceedings of AWWA Seminar on Strategies for the Control of Trihalomethanes. AWWA, Denver, CO. (127)

Croue, J-P. & Reckhow, D.A. 1989. "Destruction of Chlorination By-Products with Sulfite." Environ. Sci. Technol. 23(11):1412. (124)

Daniel, F.B.; Condie, L.W.; Robinson, M.; Stober, J.A.; York, R.G.; Olson, G.R. & Wang, S.-R. 1990. "Comparative Subchronic Toxicity Studies of Three Disinfectants." JAWWA 82(10):61. (35)

Davenport, R.J.; Wynveen, R.A. & Cooper, W.J. 1981. "Continuous, Automated, and Low-Cost Monitoring of the Organic Content in Water." JAWWA 73(10):555. (84)

Delta Islands Drainage Investigation. 1990. "Report: A Summary of Observations During Consecutive Dry Year Conditions, Water years 1987 and 1988." draft received from Bruce Agee, State of California, Department of Water Resources. (24)

Dentel. S.K. & Gossett, J.M. 1988. "Mechanisms of Coagulation with Aluminum Salts." JAWWA 80(4):187. (80)

Dempsey, B.A.; Ganho, R.M. & O'Melia, C.R. 1984. "The Coagulation of Humic Substances by Means of Aluminum Salts." JAWWA 76(4):141. (93)

Dore, M.; Merlet, N.; DeLaat, J. & Goichan, J. 1982. "Reactivity of Halogens with Aqueous Micropollutants: A Mechanism for the Formation of Trihalomethanes." JAWWA 74(2):103. (44)

Edwards, E.D.; Watson, I. & McKenna, D.C. 1990. "THM Control Using Membrane Technology - Fort Myers Case Study." Boyle Engineering Report. (consultants for AVEK Water Agency, Quartz Hill, CA). (121)

Edzwald, J.K.; Becker, W.C. & Wattier, K.L. 1985. "Surrogate Parameters for Monitoring Organic Matter and THM Precursors." JAWWA 77(4):122. (129)

Edzwald, J.K. 1986. "Conventional Water Treatment and Direct Filtration: Treatment and Removal of Total Organic Carbon and Trihalomethane precursors." in Organic Carcinogens in Drinking Water. Ram, N.M.; Calabrese, E.J. & Christman, R.J., eds. John Wiley and Sons. NY. (130)

Fecek, K.J. & Boll, J.E. 1981. "Potassium Permanganate: An Alternative to Prechlorination." Carus Chem. Corp., La Salle, Ill. (110)

Federal Register. 1975. Vol.40(248):Chapter 1, part 141. (10)

Ibid. 1979. (16)

Ibid. 1986. (17)

Feige, M.A.; Glick, E.M.; Munch, J.W.; Munch, D.J.; Noschang, R.L. & Brass, H.J. 1980. "Potential Contaminants Introduced into Water Supplies by Use of Coagulant Aids." in Water Chlorination: Environmental Impact and Health Effects. Vol. 3. Jolley, R.L.; Brungs, W.A. & Cumming, R.B., eds. Ann Arbor Sci., Ann Arbor, Mich. (76)

Fraas, T.B. 1984. Multiple Linear Regression Models for Predicting Trihalomethane Formation from Chlorinated Natural Waters. U. Arizona. Master's Thesis. (133)

Fu, P.L.K. & Symons, J.M. 1990. "Removing Aquatic Organic Substances by Anion Exchange Resins." JAWWA 82(10):70. (122)

Glaser, H.T. & Edzwald, J.K. 1979. "Coagulation and Direct Filtration of Humic Substances with Polyethylenamine." Environ. Sci. Technol. 13(3):299. (77)

Glaze, W.H. & Wallace, J.L. 1984. "Control of Trihalomethane Precursors in Drinking Water: Granular Activated Carbon With and Without Preozonation." JAWWA 76(2):68. (110)

Greenberg, A.E. 1980. "Chlorination of Drinking Water - Public Health Perspectives." in Water Chlorination: Environmental Impact and Health Effects. Jolley, R.L.; Brungs, W.A.; & Cumming, R.B., eds. Ann Arbor Sci. Pub.,Inc., Ann Arbor, Mich. (30)

Harrington, D. 1993. Professor of Biology, California State University, San Bernardino. (88)

Heath, J.; Agee, B. & Jung, M. 1989. The Delta as a Source of Drinking Water: Monitoring Results 1983 to 1987. Interagency Delta Health Aspects Monitoring Program. Dept. of Water Resources, State of California. (131)

Hewitt, E. 1974. Plant Mineral Nutrition. John Wiley & Sons., NY.

Hoehn, R.C.; Barnes, D.B.; Thompson, B.C.; Randall, C.W.; Grizzard, T.J. & Shaffer, P.T.B. 1980. "Algae as Sources of Trihalomethane Precursors." JAWWA 72(6):344. (72)

Hoehn, R.C.; Dixon, K.L.; Malone, J.K.; Novak, J.T. & Randall, C.W. 1984. "Biologically Induced Variations in the Nature and Removability of THM Precursors by Alum Treatment." JAWWA 76(4):134. (95)

Hubel, R.E. & Edzwald, J.K. 1987. "Removing Trihalomethane Precursors by Coagulation." JAWWA 79(7):98. (98)

Huck, P.M. 1990. "Measurement of Biodegradable Organic Matter and Biological Growth Potential in Drinking Waters." JAWWA 82(7):78. (66)

Hundt, T.R. & O'Melia, C.R. 1988. "Aluminum-Fulvic Acid Interactions: Mechanisms and Applications." JAWWA 80(4):176. (82)

I.M.S. 1982. "Theme Introduction: Controlling Organics - Research Update." JAWWA 74(2):57. (38)

I.M.S. 1984. "Theme Introduction: Combating Organic Contaminants." JAWWA 76(4):121. (37)

Interagency Delta Health Aspects Monitoring Program. 1989. "The Delta as a Source of Drinking Water." Department of Water Resources, State of California. (25)

J.H. "Theme Introduction: Organics." 1990. JAWWA 82(1):37. (23)

Jodellah, A.M. & Weber, W.J., Jr. 1985. "Controlling Trihalomethane Formation Potential by Chemical Treatment and Adsorption." JAWWA 77(10):95. (91)

Johnson, J.D. & Jensen, J. 1983. "THM and TOX Formation - Routes, Rates and Precursors." Proceedings of AWWA seminar on Strategies for the Control of Trihalomethanes. (41)

Johnson, J.D. & Jensen, J.N. 1986. "THM and TOX Formation: Routes, Rates and Precursors." JAWWA 78(4):156. (59)

Jolles, Z.E. ed. 1966. Bromine and Its Compounds. Ernest Benn Ltd.,London. (46)

Joyce, W.S.; DiGiano, F.A. & Uden, P.C. 1984. "THM Precursors in the Environment." JAWWA 76(6):102. (67)

Kalbus, L.H. 1993. Professor of Chemistry, California State University, San Bernardino. (45)

Kavanaugh, M.C. 1978. "Modified Coagulation for Improved Removal of Trihalomethane Precursors." JAWWA 70(11):613. (96)

Kavanaugh, M.C.; Trussell, A.R.; Cromer, J. & Trussell, R.R. 1980. "An Empirical Kinetic Model of Trihalomethane Formation: Applications to Meet the Proposed THM Standard." JAWWA 72(10):578. (48)

Knocke, W.R.; West, S. & Hoehn, R.C. 1986. "Effects of Low Temperature on the removal of Trihalomethane Precursors by Coagulation." JAWWA 78(4):189. (64)

Koch, B.; Krasner, S.W.; Sclimenti, M.J.; & Schmpff, W.K. 1991. "Predicting the Formation of DBPs by the Simulated Distribution System." JAWWA 83(10):62.

Krasner, S.W.; McGuire, M.J.; Jacangel, J.G.; Patania, N.L.; Reagan, K.M. & Aieta, E.M. 1989. "The Occurrence of Disinfection By-Products in US Drinking Water." JAWWA 81(8):41. (57)

Krasner, S.W. 1990. "Evaluation of THM Precursor Contributions from Agricultural Drains." JAWWA 82(1):57. (28)

Krasner, S.W.; Sclimenti, M.J.; Means, E.G.; Symons, J.M. & Simms, L. 1992. "The Impact of Chlorine Dose, Residual Chlorine, Bromide and Organic Carbon on Trihalomethane Speciation. Presented at the AWWA WQTC, Toronto, Canada. (20)

LaFrance, P. & Mozet, M. 1989. "Adsorption of Humic Substances in the Presence of Sodium Salts." JAWWA 81(4):155. (116)

Lange, A.L. & Kawczynski, E. 1978. "Controlling Organics: The Contra Costa County Water District Experience." JAWWA 70(11):653. (47)

Levine, A.D.; Baumann, E.R. & Lind, L.B. 1987. "Curbing THMs in Small Water Systems." JAWWA 79(5):52. (90)

Lewin, R.A. 1962. Physiology and Biochemistry of Algae. Academic Press, NY. (86)

Liao, M.Y. & Randtke, S.J. 1985. "Removing Fulvic Acid by Lime Softening." JAWWA 77(8):78. (120)

Lykins, B.W., Jr. & Griese, M.H. 1986. "Using Chlorine Dioxide for Trihalomethane Control." JAWWA 78(6):62. (112)

Lykins, B.W. Jr.; Koffskey, W.E. & Miller, R.G. 1986. "Chemical Products and Toxicologic Effects of Disinfection." JAWWA 78(11):66. (5)

Lykins, B.W., Jr.; Clark, R.M. & Adams, J.Q. 1988. "Granular Activated Carbon for Controlling THMs." JAWWA 80(5):85. (117)

M.A.S. 1990. "Theme Introduction: Toxicology." JAWWA 82(10):43. (21)

McBride, D.G. 1978. "Controlling Organics: The Los Angeles Department of Water and Power Experience." JAWWA 70(11):644. (102)

McGuire, M.J. & Meadow, R.G. 1988. "AWWARF Trihalomethane Survey." JAWWA 80(1):61. (22)

McGuire, M.J. 1989. "Preparing for the Disinfection By-Product Rule: A Water Industry Status Report." JAWWA 81(8):35. (8)

Meier, J.R. & Daniel, F.B. 1990. "The Role of Short-Term Tests in Evaluating Health Effects Associated with Drinking Water." JAWWA 82(10):48. (33)

M.F.G. 1978. "Theme Introduction: Controlling Organics." JAWWA 70(11):589. (36)

Morris, J.C. 1986. "Aqueous Chlorine in the Treatment of Water Supplies." in Organic Carcinogens in Drinking Water. Ram, N.M.; Calabrese, E.J. & Christman, R.F. eds. John Wiley & Sons, N.Y. (40)

Morrow, C.M. & Minear, R.A. 1984. "Determination of Bromide in Natural Waters by Ion Chromatography using a Concentrator Column." Water Res. 18(9);1165. (52)

Moser, R.H. & Lee, R.G. 1983. "Field Experiences with Controlling TTHMs." Proceedings of AWWA Seminar on Strategies for the Control of Trihalomethanes. (13)

MWD. 1990. "Gambling with a Water Supply." Focus 5. (A publication of the Metropolitan Water District of Southern California). (26)

Myers, A.G. 1990. "Evaluating Alternative Disinfectants for THM Control in Small Systems." JAWWA 82(6):77. (103)

Neal, R.A. 1990. "Assessing Toxicity of Drinking Water Contaminants." JAWWA 82(10):44. (32)

Ohio River Valley Sanitation Commission. 1980. Water Treatment Process Modifications for Trihalomethane Control and Organic Substances in the Ohio River. EPA pub.# 600/2-80-028.

O'Kouchi, S. & Saegusa, H. 1989. "Determination of Volatilization Coefficients of Trihalomethanes from Waters." Water Sci. Technol. 21(12):1907. (123)

Olson, B.H. 1989. "The Safety of Our Drinking Water." New England J. of Med. 320(21):1413. (4)

Pfaff, J.D. & Brockhoff, C.A. 1990. "Determining Inorganic Disinfection By-Products by Ion Chromatography." JAWWA 82(4):192. (114)

Prescott, G. 1964. How to Know the Fresh Water Algae. W.M.C. Brown, Co. Pub., Dubuque, Iowa. (85)

Randtke, S.J. & Jepson, C.P. 1982. "Effects of Salts on Activated Carbon Adsorption of Fulvic Acids." JAWWA 74(2):84.

Randtke, S.J. 1988. "Organic Contaminant Removal by Coagulation and Related Process Combinations." JAWWA 80(5):40. (79)

Rebhun, M.; Manka, J. & Zilberman, A. 1988. "Trihalomethane Formation in High-Bromide Lake Galilee Water." JAWWA 80(6):84. (42)

Reckhow, D.A. & Singer, P.C. 1984. "The Removal of Organic Halide Precursors by Preozonation and Alum Coagulation." JAWWA 76(4):151. (104)

Reckhow, D.A. & Singer, P.C. 1990. "Chlorination By-Products in Drinking Waters: From Formation Potentials to Finished Water Concentrations." JAWWA 82(4):173. (69)

Roberts, P.V. & Summers, R.S. 1982. "Performance of Granular Activated Carbon for Total Organic Carbon Removal." JAWWA 74(2):113. (119)

Roberts, P.V. & Levy, J.A. 1983. "Air stripping of Trihalomethanes." Proceedings of AWWA Seminar on Strategies for the Control of Trihalomethanes.

Rook, J.J. 1974. "Formation of Haloforms During Chlorination of Natural Waters." J. Water Trtmt. Exam. 23:234. (14)

Rook, J.J. 1976. "Haloforms in Drinking Water." JAWWA 68(3)168. (39)

Rook, J.J., Gras, A.A.; Van der Heijden, B.G. & de Wee, J. 1978. "Bromide Oxidation and Organic Substitution in Water Treatment." J.Environ.Sci.Health 13(2):91.

Scientific Panel Report. 1982. "Public Health Aspects of Sacramento-San Joaquin Delta Water Supplies." Panel assembled by the Dept. of Water Resources, State of California.

Scully, F.E., Jr.; Howell, G.D.; Jewell, J.T. 1980. "Proteins in Natural Waters and Their Relations to the Formation of Chlorinated Organics During Water Treatment." Environ. Sci. Technol. 22(5):537. (74)

Semmens, M.J. & Ayers, K. 1985. "Removal by Coagulation of Trace Organics from Mississippi River Water." JAWWA 77(5):79. (75)

Semmens, M.J.; Norgaard, G.E.; Hohenstein, G. & Staples, A.B. 1986. "Influence of pH on the Removal of Organics by Granular Activated Carbon." JAWWA 78(5):89. (97)

Sims, J.J.; Fenical, W.; Wing, R.M. & Radlock, W. 1971. "Marine Natural Products *I. Pacifenal*, a Rare Sequesterpene Containing Bromine and Chlorine from the Red Alga *Laurencia pacifica*." JACS 93:3774.

Singer, P.C.; Borchardt, J.H. & Colthurst, J.M. 1980. "The Effects of Permanganate Pretreatment on Trihalomethane Formation in Drinking Water." JAWWA 72(10):573. (108)

Singer, P.C.; Barry, J.J.III; Palen, G.M. & Scrivner, A.E. 1981. "Trihalomethane Formation in North Carolina Drinking Waters." JAWWA 73(8):392. (63)

Singer, P.C. 1983. "Applicability of Coagulants and Alternative Oxidants for Controlling THM Formation." Proceedings of AWWA Seminar on Strategies for the Control of Trihalomethanes. AWWA, Denver, CO. (92)

Singer, P.C. & Chang, S.D. 1989. "Correlations Between Trihalomethanes and Total Organic Halides Formed During Water Treatment." JAWWA 81(8):61. (60)

Singh, I.M. & McTighe, T.C. 1982. "Reducing the Formation of Trihalomethanes." Public Works 113(8):45. (83)

Smith, G.G. 1991. Manager of Operations, Antelope Valley East Kern Water Agency, Quartz Hill, California. (107)

Smith, G.J. 1990. Participant in a roundtable discussion: "Additives" JAWWA 82(10):28. (18)

Smith, Maureen M. 1988. Treatment Practices to Lower THMs: A Three Year Study. Presentation to the Antelope Valley East Kern Water Agency Board of Directors. (126)

Smith, M.M.; Harrington, D.; & Smith, G.G. 1992. "Trihalomethane Formation in Treated Surface Water Containing Bromide." Presented at the AWWA WQTC conference, Toronto, Canada.

Sorber, C.A.; Williams, R.F.; Moore, B.E. & Longley, K.E. 1982. "Alternative Water Disinfection Schemes for Reduced Trihalomethane Formation: Vol. 1. Prototype Studies." USEPA Project Summary. EPA pub. no. 600/S2-82-037. (106)

State Water Resources Control Board. 1991. "Delta Water Quality: A Report to the Legislature on Trihalomethanes and the Quality of Drinking Water Available from the Sacramento-San Joaquin Delta." State of California, Department of Health Services. (29)

Stevens, A.A.; Slocum, C.J.; Seeger, D.R. & Robeck, G.G. 1976. "Chlorination of Organics in Drinking Water." JAWWA 68(11):615. (58)

Stevens, A.A. & Symons, J.M. 1977. "Measurement of Trihalomethanes and Precursor Concentration Changes." JAWWA 69(10):546.

Stevens, A.A.; Moore, L.A. & Miltner, R.J. 1989. "Formation and Control of Non-Trihalomethane Disinfection By-Products." JAWWA 81(9):54. (101)

Stewart, W.B.P., ed. 1974. Algal Physiology and Biochemistry. U. California Press, Los Angeles. (87)

Sutcliff, J.F. 1962. Mineral Salts Adsorption in Plants. Peragamon Press, NY.

Symons, J.M.; Bellar, T.A.; Carswell, J.K.; DeMarco, J.; Kropp, K.L.; Robeck, G.G.; Seeger, D.R.; Slocum, C.J.; Smith, B.L. & Stevens, A.A. 1975. "National Organics Reconnaissance Survey for Halogenated Organics." JAWWA 67(11):634. (11)

Symons, J.M.; Stevens, A.A.; Clark, R.M.; Geldreich, E.E.; Love, O.T. Jr. & DeMarco, J. 1981. "Removing Trihalomethanes from Drinking Water." Water Eng. & Mngmt. July, p.50. (49)

Symons, J.M.; Fu, P.L.K.; Dressman, R.C. & Stevens, A.A. 1987. "The Influence of Bromide Ion on Organic Chlorine and Organic Bromine Formation During Free Chlorination." JAWWA 79(9):114. (56)

Thompson, J.C. & Amens, J.J. 1987. "Preventing the Formation of Trihalomethanes in Florida Groundwater." JAWWA 79(1):38. (115)

Trussell, A.R. & Umphres, M.D. 1978. "An Overview of the Analysis of Trace Organics in Water." JAWWA 70(11):595.

Trussell, R.R. & Umphres, M.D. 1978. "The Formation of Trihalomethanes." JAWWA 70(11)604. (15)

Urano, K.; Wada, H. & Takemasa, T. 1983. "Empirical Rate Equation for Trihalomethane Formation with Chlorination of Humic Substances in Water." Water Res. 17(12):1797. (61)

USA Today. 1989. "Toxicology: Can Chlorine Cause Cancer?" USA Today 117(2525):14. (3)

USEPA. 1988. Methods for the Determination of Organic Compounds in Drinking Water. EPA pub. # 600/4-88/039. Cincinnati, OH.

Virchem Co. "Reduction of Trihalomethanes in Potable Water Systems." Technical Data by Virchem. (62)

Watts, T.E. & Singer, R.D. 1990. "Drinking Water Contaminants: Sources, Health Considerations, and Removal." Minn. Medicine 73:33. (2)

Weber, W.J., Jr. & Jodellah, A.M. 1985. "Removing Humic Substances by Chemical Treatment and Adsorption." JAWWA 77(4):132. (94)

Werdehoff, K.S. & Singer, P.C. 1987. "Chlorine Dioxide Effects on THMFP, TOXFP, and the Formation of Inorganic By-Products." JAWWA 79(9):107. (109)

Woodard, R. & McCune, W.J. 1982. "State Water Project Trihalomethane Study." Dept. of Water Resources, State of California.

Zelibor, J.L.Jr.; Romankiw, L.; Hatcher, P.G. & Colwell, R.R. 1988. "Comparative Analysis of the Chemical Composition of Mixed and Pure Cultures of Green Algae and Their Decomposition Residues by ^{13}C Nuclear Magnetic Resonance Spectroscopy." Appl. & Environ. Microbiol. 54(4):1051. (71)

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* Number in parentheses after citation corresponds to footnote number.